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by

NEIL MALCOLM McCULLOCH

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Date 1982-04-22

ABSTRACT

The purpose of this study was to investigate the kinetics of the reverse Claus reaction,

$$2\ H_2O + 3/x\ Sx \longrightarrow 2\ H_2S + SO_2$$

This was done by obtaining space-time/conversion data at various partial pressures of sulphur and water, from which initial rates of the reaction are calculated, based on octatonic sulphur.

Kaiser S-201 catalyst, (primarily gamma-alumina) was used in an Autoclave Berty (internal recycle) type reactor. Liquid sulphur and water were vapourised and mixed with nitrogen as a carrier gas to form the feed stream. The reaction products, water and nitrogen were analysed on a sulphur-free basis by gas chromatography and an electronic integrator was used to measure the peak-areas.

A total of 173 steady state runs were performed, yielding 163 finite rate measurements and 18 initial rates. Ten initial rates were calculated at a constant water partial pressure of 3720 Pa and at partial pressures of sulphur varying from 266 Pa to 2955 Pa, which was the full range that was possible with the experimental apparatus. The remaining eight initial rates were obtained at a constant sulphur partial pressure of 756 Pa, and a variable water partial pressure, from 1537 Pa to 21,443 Pa. The balance of the feed streams was always nitrogen. For each set of experimental runs, the space velocities ranged from 50 to 220 hr^{-1} and the pressure and temperaturewere held constant at 1.46 atm ($1.479 * 10^5$ Pa) and 592 K respectively. Two more initial rates were obtained at temperatures of 624 K and 653 K, employing an additional 10 finite rate measurements.

A rate function of the form,

$$-Rw = A\,[\exp(-E/R\,T)]\,(Pw)^{a}\,(Ps_4)^{b} / [1 + K_2\,Pw]^{2}$$

where,

-Rw = rate of reaction with respect to water, mol/hr g cat,

Pw = partial pressure of water, Pa,

Ps_i = partial pressure of S_i, Pa,

was found to fit the data. The following values of the parameters were obtained,

$$A = 0.5004$$

$$-E/R = -7994$$

$$a = 0.89$$

$$b = 0.39$$

$$K_2 \quad 2.742 * 10^{-5}$$

The temperature is in Kelvin, and the partial pressures are in Pa. This rate equation was found to be consistent with earlier work by McGregor (1971) and Liu (1978), who studied the forward reaction rate at the University of Alberta. The form of the rate equation is the same as that suggested by them, and the values of the parameter K_2 obtained in this work are similar. The initial rate of the reverse reaction is less by a factor of about 10 than that of the forward reaction, which agrees with the results obtained by them for the forward reaction. However, a reaction rate equation incorporating both a forward and reverse rate term using all the finite rate data obtained was not developed. A direct comparison of the two expressions was not therefore made.

A total of 52 finite rate data at high catalyst loadings (10.0066 g) were used to estimate the maximum conversions obtainable in a Berty type reactor (CSTR). The resulting experimental conversions were found to be greater than the predicted thermodynamic conversions at the same temperature. Some possible explanations for this discrepancy were examined.

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1. INTRODUCTION

1.1 Background

Sulphuric acid is unchallenged as the world's leading industrial chemical (26,57). Indeed, its total annual production may be used as a measure of the industrial prosperity of a nation (26). It is not then surprising that, of the fifty million tons of sulphur produced annually (1976), the great majority is used in the production of sulphuric acid (57). It follows that sulphur production is a particularly important facet of the chemical industry.

During the eighteenth and nineteenth centuries, the elemental sulphur deposits found in Sicily were the main source of sulphur. Towards the end of the nineteenth century, however, the Frasch process (after its inventor, Hermann Frasch) became almost the sole source of sulphur. This process produced cheap, high purity sulphur from the unique dome deposits of Louisiana and Texas. This sulphur was of such high quality and low cost that, even when shipped across the Atlantic to Europe, it was cheaper than the conventionally mined Sicilian product (57).

At about the same time that Frasch was granted a patent for his process, a British inventor, C.F. Claus, obtained one for a process that entailed the burning of hydrogen sulphide in air over bauxite to produce elemental sulphur and water (17). This process only became industrially significant as a major source of elemental sulphur from 1960 onwards, with the development of the natural gas industry at Lacq in France and in Alberta, Canada (57). Since 1970, however, half of all the sulphur produced worldwide annually has been recovered sulphur (from hydrocarbon processing), obtained mostly by means of the Claus process (57).

The natural gas reserves of Lacq and Alberta are designated as being "sour". That is to say, they contain significant quantities of hydrogen sulphide -- in some cases as much as forty percent. This is a highly toxic and corrosive gas that readily oxidises to sulphur dioxide, which is only slightly less poisonous (57). Yet sulphur dioxide is more hazardous because it is soluble in water and forms sulphurous acid. The acid rain of environmental concern is essentially sulphurous acid (61). Clearly, sour gas is unsuitable either as a fuel or as a feedstock to other chemical processes. The Claus process has

proved to be a successful method of "sweetening" natural gas, particularly at the wellhead, so that the gas may be safely transported by pipeline to a processing plant. As a result, the process has become a major means of producing raw sulphur even though, in essence, this element is merely a byproduct of the necessary gas sweetening process.

There have been several modifications to the original process as patented by Claus (57). These have been reviewed in the next chapter. The most important modification was the splitting of the reaction into two independent steps: in the first, the hydrogen sulphide was partially burned in a waste heat boiler and in the second, the sulphur dioxide produced was reacted with the remainder of the hydrogen sulphide in a catalytic reactor. By this means, the large heat of reaction was dissipated without the damage to the catalyst which had been a problem in previous versions of the process.

The process can be summarised by the following chemical reactions :

$$H_2S(g) + 3/2\ O_2(g) \rightleftharpoons SO_2(g) + H_2O(g) \quad \ldots\ldots\ldots\ldots (1.1)$$

$$\Delta H^\circ_{298} = 520.1\ kJ$$

$$2\ H_2S(g) + SO_2(g) \rightleftharpoons 2\ H_2O(g) + 3/8\ S_8(g) \quad \ldots\ldots\ldots\ldots (1.2)$$

$$\Delta H^\circ_{298} = 108.2\ kJ$$

Sulphur vapour has been known for many years (4), to exist as several molecular species containing different numbers of sulphur atoms The basis of equation 1.2 above is octatonic sulphur. In actuality, the sulphur species may range from monotonic to octatonic and even higher, depending on the temperature and partial pressure of sulphur. As a consequence, sulphur vapour is made up of a distribution of these species. At low pressure, the vapour is almost entirely S_8 while at high temperatures, S_2 predominates. At intermediate temperatures, the distribution of species may be predicted by the Gibbs free energy of the system. McGregor (56) developed a computer program whose function was to minimise the Gibbs free energy of the sulphur system. This was revised by Truong (81) and also by Razzaghi (72) to include the "best available" thermodynamic data and also other species encountered in the Claus reaction. Many workers have reported that the equilibria predicted using thermodynamic data do not correspond to

those achieved experimentally (28,53,56). This has been considered to be due to imprecise thermodynamic data (56). The experimental difficulties in obtaining accurate data on the various sulphur species are great. The data on the odd numbered sulphur species in particular, are subject to large discrepancies depending on the source. In order to minimise the effect of such inaccuracies, the present work will consider the sulphur species S_2, S_4, S_6, and S_8 to be present in the reacting system. There is a much higher degree of unanimity between sources on thermodynamic data on these species (81). The Claus reaction then takes the following form :

$$2\,H_2S + SO_2 \rightleftharpoons 3/8\,S_8 + 2\,H_2O \quad \ldots\ldots\ldots (1.3)$$

$$2\,S_2 \rightleftharpoons S_4 \quad \ldots\ldots\ldots (1.4)$$

$$3\,S_2 \rightleftharpoons S_6 \quad \ldots\ldots\ldots (1.5)$$

$$4\,S_2 \rightleftharpoons S_8 \quad \ldots\ldots\ldots (1.6)$$

Thus, if the kinetics of the reaction are determined via equation (1.3), the equations (1.4) to (1.6) are assumed to be in equilibrium. The odd number sulphur species have been ignored, since the uncertainty in the free energy data of these species is much higher than that associated with the even number species. Using the data that are available, it is found that the odd numbered species are a small percentage of the total sulphur (72). An illustration of the difference between the two distributions is given in Appendix 2. The sulphur equilibrium reactions are assumed to equilibrate rapidly and reaction (1.3) is assumed to be rate-determining. It should be noted that, while historically the overall reaction :

$$H_2S + 1/2\,O_2 \longrightarrow H_2O(g) + 1/8\,S_8(g) \quad \ldots\ldots\ldots (1.7)$$

$$\Delta H^\circ_{298} = 628.3 \text{ kJ/mol}$$

has been called the Claus reaction, it is reaction (1.2), the catalytic reaction itself, which has come to be known as the Claus reaction, although it should more properly be referred to as the modified Claus reaction. Since reaction (1.2) is sulphur yield limiting, it shall be referred to as the Claus reaction in this work.

Further improvements to the Claus process have had the aim of increasing the sulphur yield. For example, increased yield has been achieved by means of improved boiler design (20,42), H_2S burner design (25), and control of the H_2S/air ratio (9). The development of improved catalysts (20,66) and the use of more optimal operating conditions in the catalytic reactor have also improved the yield.

Stricter regulations governing the permitted levels of sulphur emission have forced further improvements to sulphur recovery plants (57,65,66). Since impurities such as ammonia (from amine treatment plants) or hydrocarbons (for example, methane from natural gas) can significantly reduce the conversion of hydrogen sulphide, the pre-treatment of the feed stream for their removal is required. This can also greatly increase the concentration of hydrogen sulphide (16,30,31). More important than these improvements, though, has been the development of Claus tail gas clean-up units to process the Claus effluent stream even further (33,65,76,88). Such units are now used extensively and can increase the sulphur recovery from approximately 97% to over 99%.

In an exothermic reaction, the equilibrium yield is favoured by low temperatures. Decreasing the temperature also increases the sulphur molecularity towards eight. This will reduce the partial pressure of sulphur in the product stream and as a result, increase the equilibrium yield. Obviously, therefore, it is advantageous to operate the Claus catalytic reactor at as low a temperature as possible. Modern developments have been directed at taking advantage of this (32,33), even to the extent of operating the Claus converters at a temperature below the dew point of sulphur, as in the Cold Bed Absorption (CBA) process.

1.2 Purpose of this Study

The equilibrium of the catalytic reaction (1.2) has been found to be the limiting factor governing the yield in the Claus reaction. There is a significant discrepancy between the experimental equilibrium conversions obtained by several workers (4,23,28) and the conversions predicted by the "best available" thermodynamic data. It would be useful to obtain empirical data on the forward and reverse rates of the catalytic reaction in order that the equilibrium may be more accurately evaluated since at equilibrium, the forward and reverse rates are equal. With this additional knowledge, the design and

control of Claus plants may be made more precise (20).

The rate of an equilibrium reaction such as the Claus reaction will be regarded as the addition of two separate rates representing the forward and backward reactions, viz.,

$$R_{net} = R_f + R_b \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.8)$$

In the particular case of the Claus reaction, the forward reaction has been the subject of much research and this has been surveyed in Chapter (2). However, there has been no study of the reverse Claus reaction published, although it has been considered briefly in some forward reaction studies.

The purpose of this study is to determine the kinetics of the reverse Claus reaction :

$$2\,H_2O + 3/8\,S_8 \longrightarrow 2\,H_2S + SO_2 \qquad \ldots\ldots\ldots\ldots (1.9)$$

The kinetics of the forward reaction have been satisfactorily determined and the rate equation is of the form (22) :

$$-Rso_2 = k_1 \frac{(Ph_2s)^{1} \; (Pso_2)^{\frac{1}{2}}}{[1 + K_1 Pw]^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.10)$$

It is the intention of this study to seek a comparable expression for the reverse reaction. If the rate expression is to exhibit thermodynamic consistency with equation (1.10) above, a form such as equation (1.11) is suggested :

$$-Rw = \frac{k_2 (Pw)^{a} \; (Ps)^{b}}{[1 + K_2 Pw]^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.11)$$

The above equations apply individually, only to the special case of the initial rate of reaction, where no products are present to take part in the appropriate reverse reaction. The forward and reverse rate expressions may be combined in a general

equation of the following form, which represents the overall rate of the Claus reaction :

$$Rw = \frac{k_1 (Ph_2s)^c (Pso_2)^d - k_2 (Pw)^a (Ps_t)^b}{[1 + K_1 Pw]^2} \quad \ldots\ldots\ldots (1.12)$$

The parameters K_1 and K_2 will be equal since they represent the adsorption equilibrium constant of water and hence will be a function of the temperature only.

This empirical expression may be useful in the design and control of Claus plants.

1.3 Experimental Approach

An equilibrium reaction is perhaps most easily investigated by using the method of initial rates. This approach was employed by McGregor (56) to investigate the forward Claus reaction. The initial rate is that rate of reaction which occurs in the absence of any products, that is :

$$-Rw = k\, Pw^a\, Ps_t^b \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.13)$$

By obtaining finite rate data at various space velocities, it is possible to derive the initial rate. The data is extrapolated to obtain the rate at zero conversion. The theoretical analysis is outlined in Chapter four. Once the initial rates have been determined, the parameters of the rate equation may be derived by applying a combination of linear and non-linear regression analyses to an assumed form of the rate expression. There are three effects studied in this work : The variation of the rate of the reverse reaction with (1) the partial pressure of sulphur; (2) the variation of the rate with partial pressure of water; (3) the effect of temperature on the rate.

2. LITERATURE SURVEY

2.1 Introduction

Although the literature contains many references to the Claus process, these are in the main of a descriptive rather than a theoretical nature. This survey will concentrate on that section of the literature which is pertinent to the kinetics of the Claus reaction itself. Other aspects of the Claus process have been extensively reviewed elsewhere, notably by Truong (81), Liu (53), Cho (15), Liu (52), and McGregor (56). Other reviews are available for the period up to 1970 by Pilgrim and Ingraham, (69) and for 1970–75 by Chandler (13).

2.2 The Claus Reaction

The reaction,

$$H_2S + 3/2\ O_2 \longrightarrow \text{sulphur} + \text{water} \qquad \ldots\ldots\ldots\ldots (2.1)$$

had been well known as a laboratory demonstration reaction from the early nineteenth century (18), but it was C.F. Claus who, in the 1880's, first designed a commercial process using it (17). His patent of 1887 describes a process for the recovery of elemental sulphur from calcium sulphide. The sulphide, when treated with carbonic acid, produces hydrogen sulphide which subsequently reacts with air over one of several catalysts, including bauxite, to produce sulphur.

In 1887, the Chance brothers (12) were granted a patent for a commercial process for the recovery of elemental sulphur from the waste gases of the Le Blanc process (57). This process for producing sodium carbonate was responsible for a great deal of the pollution in nineteenth century England during the height of the Industrial Revolution (26). The Chance application of the Claus process represents its first use in the field of pollution abatement.

Reaction (2.1) is highly exothermic, however, and the Chance–Claus process proved very difficult to control (69). As a consequence, in 1937, I.G. Farbenindustrie modified the process and effectively eliminated the problem of temperature control (2).

This was achieved by burning one-third of the hydrogen sulphide with air in a waste heat boiler, and producing sulphur dioxide. This sulphur dioxide was then reacted with the remainder of the hydrogen sulphide to produce the final products, elemental sulphur and water. Hence the original reaction takes place in two stages:

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O \quad (1000\ ^\circ C) \qquad \ldots\ldots\ldots\ldots (2.2)$$

$$\Delta H = 520 - 577\ kJ$$

$$2\ H_2S + SO_2 \longrightarrow 2\ H_2O + 3/x\ Sx \quad (250\ ^\circ C) \qquad \ldots\ldots\ldots\ldots (2.3)$$

$$\Delta H = 88 - 130\ kJ\ [1]$$

The major fraction of the total heat of reaction is thus dissipated in the furnace section. This process became known as the modified Claus process, and is the basis of all present Claus plants.

2.3 Claus Reaction Kinetics

The adoption of the Claus process as a primary method of desulphurisation of natural gas and, as a result, of sulphur production, has prompted research on the kinetics of the Claus reaction.

Pilgrim and Ingraham (69) reviewed the process and its kinetics up to 1970, while Chandler (13) reviewed subsequent developments between 1970 and 1975. The emphasis, however, of these reviews is on the practical aspects of the process itself.

The first reference to the reaction in the literature is by Cluzel (18) in 1812. He noted that no sulphur would be produced if the gases were first dried by passing them over calcium chloride. Lewis et al., (49,51,70) studied the equilibrium of the H_2S/SO_2 system in a series of papers. Their work, published in 1918, demonstrated that the reaction is reversible and also that it is heterogeneous. The rate of the reaction was reported as being high in both directions. An equilibrium constant was calculated, but this was subject to large deviations.

---

[1] The heats of reaction are given as ranges since they represent the actual process reactions. The temperatures and pressures are not therefore precise. The distribution of sulphur species will also be subject to variation.

The first quantitative work was performed by Taylor and Wesley in 1927 (79). This work confirmed the heterogeneity of the reaction. Despite reported difficulties in analysing the reaction products, and in particular, determining the sulphur partial pressure, they ventured an estimate of the rate equation for the reaction on glass, which they reported to be of the form :

$$-Rh_2s = k\,(Ph_2s)^{1.5}\,(Pso_2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.4)$$

The authors discussed what the nature of the reaction mechanism was likely to be but this was essentially speculation since, at that time, there was a dearth of experimental data on the adsorption of the various species on glass.

In 1937, Undintseva and Chufarov reported (83,84) that hydrogen sulphide and sulphur dioxide would not react homogeneously at temperatures between 250 and 350 °C. They also found glass, aluminium, and aluminium oxide to be good catalysts. In addition, iron and iron oxide were reported to exert only a weak catalytic effect.

Murthy and Rao (62), in 1952, studied the reaction over metallic sulphide catalysts using a batch recycle reactor at 25 °C. The condensation of sulphur on the catalyst prevented steady state from being attained since the surface area of the catalyst was changing. They reported that, at this temperature, the reaction would not proceed with any of the catalysts tested unless water was present.

The work of Gamson and Elkins, reported in 1953, represents the first comprehensive study of the Claus reaction (28). The reaction was studied in an integral reactor over Porocel catalyst (an activated bauxite). Space time versus conversion data were obtained but no attempt was made to derive a rate equation. A hypothetical sour gas plant feed stream, comprising 6.75% H_2S, 3.39% SO_2, 26.83% H_2O, and the balance, N_2, by volume, was used. Four space velocities, and three temperatures ranging from 230 to 300 °C, were employed. The authors were careful to caution that the kinetic data of this study were inconsistent with their thermodynamic analysis of the Claus reaction in that the experimental conversions were higher than those calculated from free energy data.

In 1957, Hammar (38) studied the reactions involved in a sulphur plant technology, using a glass differential reactor. He failed, as had his predecessors, to derive a rate

equation for the Claus reaction.

Cormode, in 1965, studied the Claus reaction using a recycle flow reactor containing Porocel catalysts (19). He suggested that H_2S itself was decomposing in his apparatus but the analysis was not precise enough to allow him to come to a firm conclusion.

Munro and Masdin (60) reported, in 1967, that water significantly retarded the rate of reaction. This effect was attributed to Le Chatelier's principle. They employed activated alumina and molecular sieve as catalyst, over the temperature range of 100–300 °C at a space velocity of 70 vol H_2S/cat vol hr. The water content in the feed was varied from 5 to 20 %.

Landau et al., (47) concluded in their results, published in 1968, that diffusional effects were rate limiting. Unfortunately, they did not state whether pore or film diffusion was occurring and, in addition, they did not describe their experimental equipment nor the catalyst charge sizes. It is impossible, therefore, to determine what type of diffusion, if any, was occurring.

A report by the Allied Chemical Corporation in 1970 (1) on Claus process kinetics contains a comprehensive literature survey. A dynamic flow system and Porocel LPD catalyst were used. The experimental conditions were varied over the following ranges : the temperatures were between 200 and 370 °C, residence times between 0.125 and 2.50 seconds, and feed concentration of H_2S between 1 and 6 %. It was reported that the rate of reaction was so fast that equilibrium was attained within 0.5 seconds. The observed equilibrium was found to be higher than that which had been predicted using a mathematical model that considered the sulphur vapour to be composed solely of S_8. The following rate constant for the reaction was derived ;

$$k = 61.66 \exp(-1305/T) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.5)$$

assuming the reaction to be first order in all reactants. The temperature was measured in Kelvin, but pressure units were not given and a full rate equation was not developed.

The work of Struck et al., (74) was carried out at low temperatures, below the sulphur dew point. The reaction was found to go almost to completion, in accordance

with the predicted thermodynamic equilibrium at these temperatures. At 182 °C, the achieved conversion was higher than that predicted, and at 100 °C, the conversion was close to 100%.

The first serious attempt to derive a rate equation for the Claus reaction was made by McGregor in 1971 (56), as part of an extensive programme of research being carried out at the University of Alberta. In a series of 80 experiments involving the use of an external recycle reactor containing Porocel catalyst, the reaction was studied by means of initial rate experiments over the range 208–287 °C. The following parameters were derived :

$$\text{Ea} = 7589 \pm 451 \text{ cal}$$

$$\text{order wrt } H_2S = 0.828 \pm 0.0951$$

$$\text{order wrt } SO_2 = 0.417 \pm 0.111$$

Various mechanistic equations were fitted to the data but no attempt was made to discriminate between the models. Water was observed to exhibit a barely perceptible autocatalytic effect at low partial pressures, and a marked retardation at high partial pressures. The catalytic activity was found to vary with the external area of the catalyst pellets, and it was concluded that the reaction took place primarily on the exterior surface of the catalyst. Finally, no evidence of a homogeneous component to the rate of reaction was found.

By applying non–linear data reduction techniques to all the available data, an empirical rate expression incorporating a reverse reaction term was obtained :

$$-R_{SO_2} = 1.292 \exp[-7100/RT] [(P_{H_2S})^{0.904} (P_{SO_2})^{0.475} - 0.504 (P_W)^{0.982}] \quad \ldots (2.6)$$

However, as the variances were large, there was a need for more data.

The empirical expressions derived by McGregor were found to correlate the data as well as any of the mechanistic models he proposed. The results reported by Hammar and by Cormode were compared with it. The expressions of Hammar (38) correlated the

data well, although the actual data could not be compared. The work of Cormode (19) was in reasonable agreement, though the actual rates were higher.

In 1972, Karren (39) was unable to obtain steady state reaction data because he found that the liquid sulphur collected by the sulphur condenser catalysed the reaction. The retarding effect of water was noted, as was the extent of sulphur loading on the catalyst.

Dalla Lana et al., in 1972, took the data analyses of McGregor further (22), and concluded that, on statistical evidence, the reverse reaction term of equation (2.5) could not be justified. They postulated that the retarding influence of water was more likely to be due to adsorption of water on the catalyst. They derived a different equation using McGregor's data :

$$-Rh_2s = \frac{Ae}{Ap}\ 1.121\ \exp[-7440/RT]\ \frac{(Ph_2s)\ (Pso_2)^{0.5}}{[1 + 0.00423\ Pw]^3} \qquad \ldots\ldots\ldots\ (2.7)$$

The term Ae/Ap was introduced by McGregor to allow for variations in specific surface area between different catalysts or even between different forms of the same catalyst. The orders of the reaction with respect to H_2S and SO_2 were rounded off to agree with the stoichiometry of the reaction.

In 1978, George (30) performed an initial rate study of the Claus reaction using cobalt molybdate catalyst. A fixed bed integral reactor was used. A temperature range of 240–450 °C and pressures of up to 1.3 atmospheres were employed. The following rate equation in the form of equation (2.6) above was developed :

$$-Rso_2 = k_1\ (Ph_2s)^1)/\ [1 + 0.10\ Pw] \qquad \ldots\ldots\ldots\ (2.8)$$

The actual experimental orders were :

$H_2S \longrightarrow 0.93 - 0.96$

$SO_2 \longrightarrow 0.02 - 0.08$

The activation energy was found to be :

$Ea = 5.5$ kcal/mol

It was concluded that sulphur did not catalyse the reaction as had been suggested by Hammar (38). Water again retarded the reaction and this effect was allowed for by the adsorption term, (the denominator) in equation (2.7). In addition, film diffusion effects were found to be negligible and it was suggested that pore diffusion was significant.

From his experiments in 1975 to evaluate a copper-doped catalyst Cho (15) concluded that conversions greater than the theoretical equilibrium were obtained. The effect of external concentration gradients was negligible. The reverse reaction was thought to be significant although its visible rate was negligible.

Dalla Lana et al. (21) derived, in 1976, a rate equation for the Claus reaction using data obtained by Liu in his work on the pure gamma alumina catalyst.

$$-Rso_2 = 0.460 \exp[-7350/RT]\ (Ph_2s)\ (Pso_2)^{0.5} / [1 + 0.006\ Pw]^2 \quad \ldots\ldots\ldots\ldots (2.9)$$

This equation is nearly identical to that derived from McGregor's study (22). The similarity between equations (2.6) and (2.8) was remarkable since each was derived from data on two different catalysts.

The likely mechanism of the reaction was investigated and a Langmuir-Hinshelwood rate expression was derived, based on the following surface reaction step which was considered irreversible and rate controlling :

$$H_2S.Al^* + O.Al^* \longrightarrow H_2O.Al^* + S.Al^* \quad \ldots\ldots (2.10)$$

where Al^* is a lewis acid site on the catalyst surface.

The postulated mechanism led to the following rate equation :

$$-Rso_2 = k\ (Ph_2s)\ (Pso_2)^{1/2} / [Psn/K_4]^{0.5/n}\ [1 + Pw/K_3]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.11)$$

where n, the average size of the sulphur molecule, is approximately 7. The sulphur term is then negligible and the expression is similar to equation (2.8).

Kerr et al. in 1976, reported that they had found a second order equation to apply in their experiments involving bauxite and activated alumina catalysts (42). This was reported as being,

$$d(H_2S)/dt = -k_f [H_2S] [SO_2] + k_b [H_2O] [Sn] \quad \ldots\ldots (2.12)$$

where,

$$k_f = 24149 \exp[-2526/T]$$

and,

$$Ea = 5.02 \text{ kcal/mol}$$

The experiments were carried out in a macroscopic vessel under isothermal conditions with flow rates, temperatures, compositions, and pressures corresponding to those attained in the second, third, or fourth catalytic converters of an industrial plant.

In 1977, Blanc et al. (8) developed an essentially empirical reaction model which included terms to account for the reverse reaction. The equation was given without units :

$$-Rso_2 = k \exp[-E/RT] \quad \frac{(Ph_2s)\,(Pso_2)^{0.5} - (1/K^{0.5})\,(Pw)\,(Ps)^{0.5}}{[1 + C\,(Pw)]^{0.5}} \quad \ldots\ldots\ldots (2.13)$$

where,

$$K = \frac{(Pw)^2\,(Ps)}{(Ph_2s)^2\,(Pso_2)}$$

This equation was applicable at temperatures greater than 270 °C. The power of the denominator term could be varied over a large range without the sum of the squared deviations between the experimental and the computed values changing greatly. This was explained by the fact that the factor multiplying the water adsorption term, and the power of the denominator are very highly correlated.

The catalyst used by Blanc et al. was activated alumina, type 5-10, and the data were collected over the temperature range 270-370 °C. Feed concentrations of H_2S ranged from 2.5 to 10 %, while the ratio of SO_2 to H_2S ranged from 0.4 to 0.6. The amount of water in the feed was varied from 5-35%. General results were as follows : the overall order is greater than 1 ; the order with respect to sulphur is not zero ; the

overall rate increases with temperature ; the activation energy is small ; water vapour favours the reverse reaction and decreases the forward reaction ; the reaction is very fast ; there are no film diffusion effects ; and pore diffusion effects are apparent.

In 1978, Liu (53) studied the Claus reaction as catalysed by gamma-alumina (Alon), using a recycle reactor and employing infra-red analysis to measure the reaction rate. The following rate equation was derived :

$$-Rso_2 = \frac{b_{10}\exp[-E_{10}/RT\,](Ph_2s)\,(Pso_2)^{0.5}}{[1 + b_{20}\exp(-E_{20}/RT)\,(Pw)]^2\,(Ps_x)^{0.5}} \qquad \ldots\ldots\ldots\ldots (2.14)$$

where,

$b_{10} = 9.72 * 10^{-5}$

$b_{20} = 1.15 * 10^{-5}$

$E_{10}/R = 3509 \pm 254$

$E_{20}/R = 3158$

This equation is very similar to that developed by McGregor, who used the Porocel (bauxite) catalyst.

Evidence of the reverse reaction was sought by introducing Claus reaction products. Since hydrogen sulphide and sulphur dioxide were not subsequently detected, it was concluded that the reverse reaction was negligible. This test was performed at 210 and 320 °C. The nitrogen flow used was 40 ml/min. with saturated sulphur at 300 °C. Water was introduced at $1.95 * 10^{-4}$ gmol/min. The model developed by McGregor was found to correlate this data well. The term $(Ph_2s\,(Pso_2)^{1/2})$ was found to be vital to a good fit. Water was observed to have a significant retarding effect on the reaction, as did sulphur. Film diffusion was negligible and it was concluded that pore diffusion could be disregarded providing the catalyst weight was below 250 mg.

In 1978, Grancher (34,35) reported on the work performed by the Aquitaine research group at Lacq in France. A rate expression was determined, but it was not reported in these papers. The author reported that the expression had the following features: the order with respect to H_2S was 1, and with respect to SO_2, 0.5; and there

was inhibition due to water. The reaction was reported to be limited by internal diffusion resistances. The validity of the model was checked by comparison with the Lacq plant itself.

Finally, the paper by Liu et al., published in 1980 (50), summarises the state of the art with respect to kinetics studies of the Claus reaction. The authors conclude that use of a rate equation is an aid in making process calculations and that these are "sensitive" to the various rate expressions. In particular, the reliability of these rate expressions is increased when they are based on surface chemistry studies. There is still, however, no reliable method for predicting either the thermodynamic properties or the dynamics of the sulphur vapour equilibrium, and this is a liability. Liu's final conclusion is that the particular catalyst used is merely a matter of preference, unless special conditions otherwise dictate. For example, the presence of hydrocarbons in the feed stream may introduce significant quantities of carbon sulphides, CS_2 and COS. If this is the case, it would be advantageous to employ a catalyst which promoted the decomposition of these species in addition to catalysing the Claus reaction.

3. EQUIPMENT DESCRIPTION AND OPERATION

3.1 Introduction

This experimental study is essentially similar to that performed by McGregor (56) in his study of the forward reaction in that an initial rate study was made of the Claus reaction system. There are, however, several important differences. In particular, the reactants, water and sulphur, are not vapours at room temperature and pressure. As a result, the feed and reactor are different. Several different versions of the experimental equipment were employed in an effort to determine which, with respect to smoothness of flow, ideal mixing, et cetera, was the most satisfactory. The most successful is shown in Figure 3.1 below. The salient features of some of the alternative systems employed are discussed in the final section of this chapter. This is the system used to obtain the rate data of this study. Another significant difference between the McGregor study and this one is the use of a Berty-type internal recycle reactor. The external recycle reactor of McGregor's work has several disadvantages for the water/sulphur reaction system. The merits of the Berty reactor vis-a-vis the external recycle reactor will be discussed in detail.

3.2 Experimental System

A diagrammatic representation of the experimental system is shown in Figure 3.1. It shows a stream of dry nitrogen which is pre-heated to 375 °C in an oven [11] [2]. Liquid sulphur from a syringe pump [10] is added in the same preheat oven [11]. The temperature is above the sulphur dew point and the sulphur vapourises. The water component is added by a syringe pump [12] and is heated to the temperature of the feed line and vapourised. It is then added to the feed stream immediately before it enters the reactor [13]. The reactor effluent is passed to a sulphur condenser [14] which eliminates most of the unreacted sulphur. The product stream is then split, with a small portion of it being led to the gas chromatograph by way of a final sulphur condenser [15], and then is expelled through a vent to the atmosphere.

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[2]The numbers in square brackets following an item of equipment refer to Figure 3.1.

Figure 3.1 Experimental System

Equipment List

1. Nitrogen cylinder
2. Drier
3. Rotameter
4. Needle valve
5. Differential flow controller
6. Feed pressure and temperature sensors
7. Differential pressure cell
8. Feed control valve
9. Reactor pressure sensor
10. Sulphur syringe
11. Preheat Oven
12. Water syringe feeder
13. Berty reactor
14. Sulphur condenser
15. G.C. secondary condenser
16. Secondary sulphur condenser
17. Water condenser
18. Reactor pressure control valve
19. Sulphur Syringe Reservoir
20. Sulphur Syringe Oven

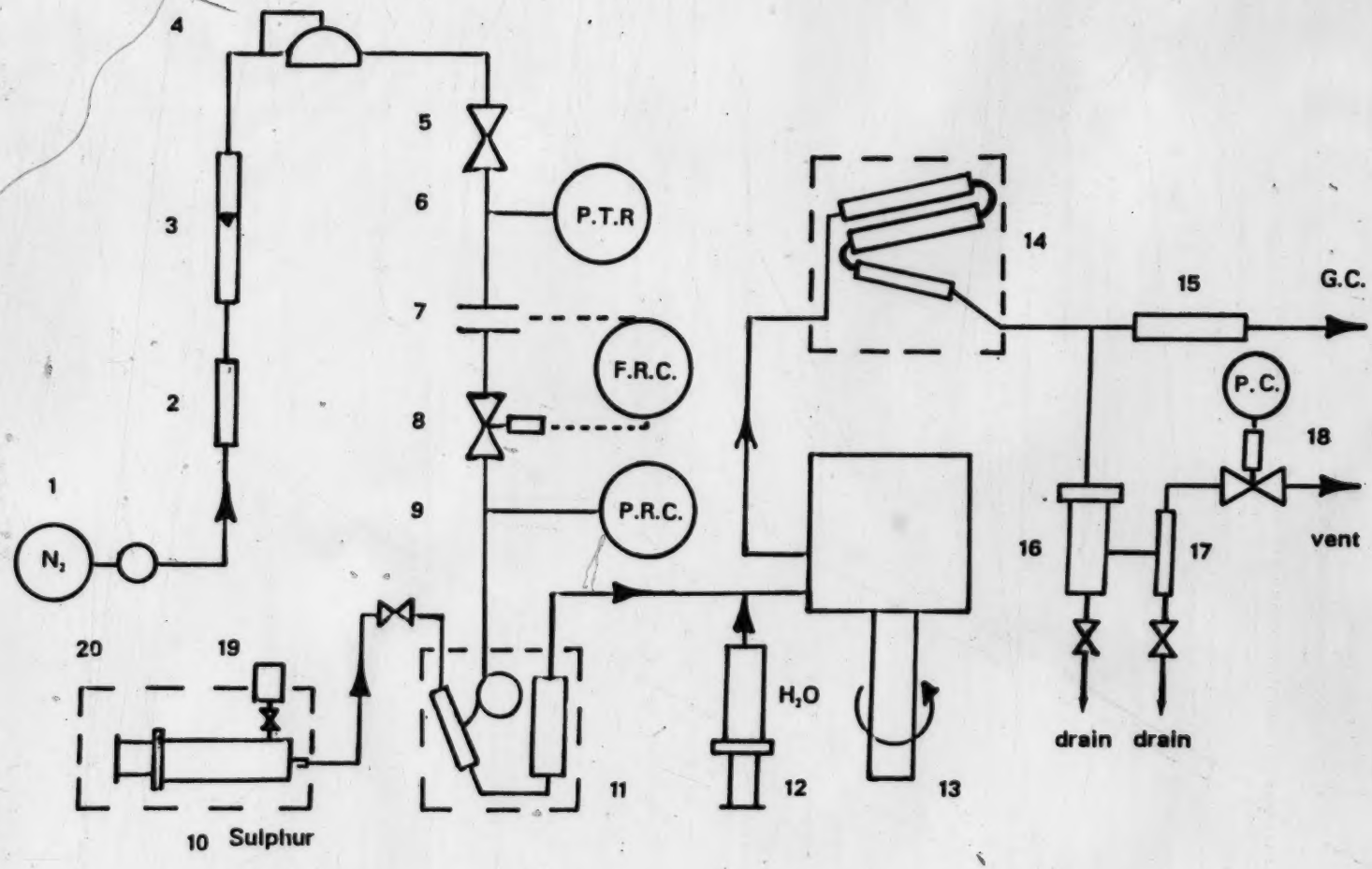


Figure 3.1 Experimental Equipment

The main stream continues through to a final sulphur condenser [16] and a water condenser [17] before being vented via a control valve [18] to the atmosphere.

The system had several drawbacks and some advantages which will be elaborated upon in the individual sections below.

3.3 Nitrogen Feed System

Linde Gas Products high purity nitrogen was regulated to 60 lb/in^2 [1], a pressure which was adequate for the entire range of flow rates employed. Each new nitrogen cylinder was analysed for oxygen using the gas chromatograph. A molecular sieve column was used at room temperature. Every nitrogen cylinder was found to be free of oxygen contamination using this method. A single peak was the only response, indicating that nitrogen only was present. The nitrogen was passed through a 12 inch bed of calcium sulphate [2] in order to remove any water that was present. A small amount of "drierite" [calcium sulphate coloured with cobalt] was used as an indicator of the efficiency of this operation. It was found unnecessary to replace the calcium sulphate. The stream was then passed through a Matheson rotameter [3] of tube size 602. The valve of the rotameter was kept fully open and the rotameter served only as a visual indicator of the flow. Immediately after the rotameter, a Nupro needle valve [4MG] was employed [4]. This valve provided the fine metering of the nitrogen flow. A Moore differential flow controller [63SD-L] was placed downstream of the needle valve to smooth any small fluctuation in flow [5]. This type of controller provides constant mass flow independent of pressure changes.

The temperature and pressure of the nitrogen feed stream were measured [6] immediately before the differential pressure cell [7] which measured the volumetric flow. Temperature was measured using an iron-constantan thermocouple, and pressure by means of a USG pressure gauge, which was accurate to 0.1 psig. The volumetric flow rate was measured by a Foxboro differential pressure cell [613 DL] and controlled by a Foxboro controller and monitored by a Foxboro chart recorder. Volumetric flow rates of between 0-2 litres per minute at a pressure of 8.5 psig were obtainable.

The nitrogen stream was then fed into the preheat oven [11] where it was passed through a 12 foot coil of 1/8 inch stainless steel tubing and was preheated to 375 °C

before it was led to the sulphur mixing vessel.

3.4 Sulphur Feed System

The sulphur component of the feed was added by means of a liquid syringe feeder driven [10] by a constant speed motor . The liquid sulphur was led into the preheat oven [11] which was maintained at a temperature of 375 °C, where it entered a mixing vessel via a syringe-type nozzle and contacted the preheated nitrogen. This mixture then entered a surge tank to allow it to equilibrate.

The cylinder of the sulphur syringe had an internal diameter of 1 inch and a working length of 5 inches. The entire syringe [10], including the reservoir [19], was enclosed in a temperature-controlled oven [20] that was maintained at 140 °C. This temperature was chosen to ensure that no plugging occurred at the oven exit and also to maintain the liquid sulphur in the low-viscosity state. Sulphur undergoes molecular restructuring at about 159 °C and there is a dramatic increase in viscosity (80).

The sulphur syringe was filled from a liquid sulphur reservoir [19]. The reservoir was sealed from the syringe by a valve. A second valve was inserted between the syringe and the mixing oven. This arrangement allowed an on-stream refilling of the syringe which disturbed the steady-state conditions only momentarily. This arrangement also ensured that no air would enter the syringe while it was being filled with sulphur. The seal of the syringe piston was made using two teflon "O"-rings. The material of construction was 316 stainless steel. The reservoir valve was a Whitey ORM2, rated to 232 °C. The syringe valve was a Whitey SS-NBS4-HTP, rated to 316 °C.

The syringe pump itself was driven by a constant speed motor. This drove a gear train which could be altered to supply any one of six different speeds. The rotary motion of the gears was translated into horizontal displacement of a push rod by means of a worm gear. For the arrangement of the gears, see Figure A-1.1 in Appendix 1.

3.4.1 Operation

Over a period of time, it was found necessary to replace the teflon "O"-rings because they tended to wear. Great care was taken to ensure that no air remained in the syringe after the replacement of the "O"-rings was complete. This was achieved by repeatedly filling the syringe with sulphur and then expelling it into the reservoir. This was done a minimum of three times. An added precaution was taken by filling the reservoir only as required, shortly before refilling the syringe itself. Additional problems were encountered due to the reservoir valve leaking and this required replacement on two occasions.

3.5 Water Feed System

A Sage Instruments model 355 syringe pump [12] was used to add the water component of the feed stream. A 20 ml syringe was used for all runs. This size was sufficient to supply water for at least one run, and yet was small enough that the back pressure was not so great that it slowed the pump. In contrast with the sulphur feed, the water flow could be adjusted fractionally over a wide range of flow rates (*vide* Appendix 1)>. The water was vapourised by heating the final 10 cm of the water line to the temperature of the reactor feed line, about 325 °C. The water was then added to the nitrogen and sulphur stream at its point of entry into the reactor [13].

The mixing of the two streams was achieved using a Swagelok "T" fitting. A section of 1/16th inch tubing was used to introduce the vapourised water directly into the centre of the main feed stream via a syringe-type nozzle. Perfect mixing of the feed stream was ensured by operating the reactor at high speed, at or above 1200 rpm. This was checked by conversion versus speed tests, (*vide* Preliminary Experiments, Section 4.2).

3.5.1 Operation

The syringe pump itself was found to perform satisfactorily in all ranges. There was a need, however, to keep the water flowing long after the sulphur flow had been stopped to prevent the sulphur back diffusing up and plugging the 1/16th inch tubing which served to deliver the vapourised water.

3.6 Reactor

There are a wide choice of reactor types available to the researcher in the field of chemical reaction kinetics (10,73). The reasons why a particular reactor is chosen depend on a large number of factors including the nature of the reaction, the type of data required, and the reaction regime that is of interest. Several reviews have been published to aid in the discrimination between the various reactors (3,43,75). Carberry (11) suggests that the "ideal" laboratory reactor for the study of catalytic kinetics is one which operates isothermally over a wide range of conversions at steady state and with a well-established residence time, while facilitating the direct determination of the rate law. Accepting these criteria, it appears that the continuous stirred tank reactor has the most suitable characteristics. As a consequence, much effort has been devoted to designing laboratory reactors which approach continuous stirred tank (CSTR) operation, and which will also accommodate a heterogeneous catalytic reaction. Kiperman (44), credits Temkin with first proposing the term "gradientless reactors" for these reactors, since the quality of being well mixed ensures the elimination of both temperature and intraphase concentration gradients.

3.6.1 Gradientless Reactors

The use of gradientless reactors in particular, has been reviewed by Sunderland (75) and Kiperman (43). The first reactor of this type was the external recycle reactor in which a pump recirculates a fraction of the reactants through a packed bed. The studies of McGregor (56) and Liu (52) at this university were performed using a reactor of this type. Butt et al. (9) and Perkins and Rase (68) discuss the use of this particular type of reactor.

The external recycle reactor has several disadvantages. The external tubing and pump represent considerable dead volume compared to the volume of the packed bed. This results in long residence times which may be undesirable, especially in the kinetic study of a fast reaction. Also, depending on the temperature of the reaction, it may be necessary to cool the recycle stream before it reaches the pump and reheat it before it enters the reactor. This would be awkward, especially if there were a danger of one of the components condensing at a cold spot in the recycle loop, as in the case of the

partial oxidation of methanol to formaldehyde (27). In this reaction, the paraformaldehyde may condense (27). Obviously, this may be a problem with reverse Claus reaction studies, since not only are high temperatures involved (> 600 K), but significant sulphur partial pressures are also employed. Sulphur is notorious for its tendency to condense at inconvenient places.

In order to avoid the limitations of the external recycle reactor, internal recycle reactors were developed. The first such was the so-called Carberry, or spinning basket reactor (Tajbl et al, 78). This reactor is similar to the simple CSTR except that the agitator is constructed to form a basket in which the catalyst is contained. Such a reactor was designed and built in this department by Turner (82) who also described its operation. The main disadvantage of this reactor is that it is impossible to arrange the catalyst and baffles, et cetera, to ensure that each catalyst pellet is equally accessible to the reactant phase since there are inevitably velocity gradients in such a mixed vessel.

The inherent problems of both the external recycle and the spinning basket reactors may be eliminated by using an internal recycle reactor. There are many reactors of this type, and most have the common feature that the vapour has a definite path for circulation around the reactor vessel, during which it passes through a packed bed. These reactors have been reviewed by Bennet et al. (3) and by Sunderland (75). Each variation on the internal recycle theme has its own particular merits and demerits.

The reactor developed by Berty et al. (6) was adopted for this study since this reactor is well documented (5,6,55) and, most importantly, the spinning basket reactor (SBR) developed by Turner (82) could be adapted to the Berty reactor configuration relatively easily. An important advantage of the Berty reactor, although not used in this study, is that it is possible to measure, or calculate, the actual mass velocities through the catalyst bed and thus reproduce, if desired, industrial reactor conditions . The mass velocities may be calculated by directly measuring the pressure drop across the catalyst bed and using Leva's or some similar correlation. This was the method used by Berty et al. (6) to evaluate the performance of this type of reactor.

3.7 Berty Reactor

The spinning basket reactor of Turner was converted to a Berty reactor by extending the reactor casing and fitting internal baffles and an impeller. Extensive experimentation using a full size Lucite model determined that a forward curved bladed impeller performed best, though high speeds of over 2500 rpm were required to achieve visible flow through the packed bed even at a low catalyst loadings (1-2 g). To achieve the required flow pattern, it was found that the clearance of the impeller had to be as low as possible so that bypassing of the catalyst bed was reduced to a minimum. This testing was performed using a hot wire anenometer with smoke from hot solder flux, as an indicator of flow. The Turner SBR system could be operated at speeds of up to 4000 rpm and it was anticipated that this would be well in excess of that required to ensure ideal Berty reactor operation. The residence time distribution of the reactor was assessed by using a He pulse and checking the response with a gas chromatograph. This test indicated that ideal mixing was achieved at speeds as low as 500 rpm. A subsequent test, however, in which conversion was plotted against impeller speed, indicated that this was due to simple mixing with bypassing, and not to circulation. The results of the conversion vs. rpm test determined that ideal mixing and circulation could be ensured only at impeller speeds of greater than 3000 rpm.

Attempts to obtain steady state kinetic data were frustrated because the catalyst activity appeared to increase over the course of even one run. This was found to be due to carbon dust originating from the lower high-temperature graphite bearing, entering the reactor and providing additional catalytic material. The stainless steel shield whose use was recommended by Turner, had been installed but the wear on the bearing was too great and the dust overloaded the shield. It would have been desirable to reduce the impeller speed -- by increasing the impeller diameter, for example -- but the reactor oven was too small and this was not possible. Ultimately, the frequency of maintenance that was required to clean the reactor vessel and also replace the carbon bearing made it desirable to use another reactor.

An Autoclave Berty type reactor was obtained to replace this reactor. This reactor was similar to that developed by Berty et al. (6), and used by Mahoney (55) in studies of n-heptane isomerisation. It was further evaluated by Berty (5). This is the

reactor shown in Figure 3.2 and its specifications are :

Volume = 664cm³
Catalyst Volume = 25.7 cm³
Max RPM = 1500
Max Pressure = 2000 psi
Max Temperature = 2500 K
Catalyst Bed Diameter = 2.54 cm
Impeller Diameter = 10.16 cm

Kuchcinski and Squires (46) have developed an empirical set of equations for use in determining whether or not the Berty reactor will function properly (i.e. without significant temperature and concentration gradients), during low pressure operation. Berty (5) had suggested that, because at low pressures and corresponding low gas densities it is difficult to maintain sufficiently high mass velocities in the reactor, in order to eliminate temperature and concentration gradients, a lower pressure limit of 45 psig ($3.1 * 10^5$ Pa) should be observed. The mass velocity of the gas through the catalyst bed governs the thickness of the stagnant boundary layer at the catalyst surface and in order to maintain gradientless conditions , high mass velocities are necessary. Kuchcinski (46) had established that the Berty reactor could operate satisfactorily at 1 atmosphere by examining the reactor performance in the reaction of CO with O_2.

The equations that Kuchcinski and Squires derived were based on the following reasoning :

If an adiabatic catalyst bed is assumed and the conditions are at steady state, the heat generated by the reaction is equal to the heat removed by the gas phase,

$$\dot{n}\,\Delta H = \dot{m}\,Cp\,\Delta T$$

Using the Colburn j factors (90), the mass and heat transfer coefficients can be estimated and the heat and mass balances yield.

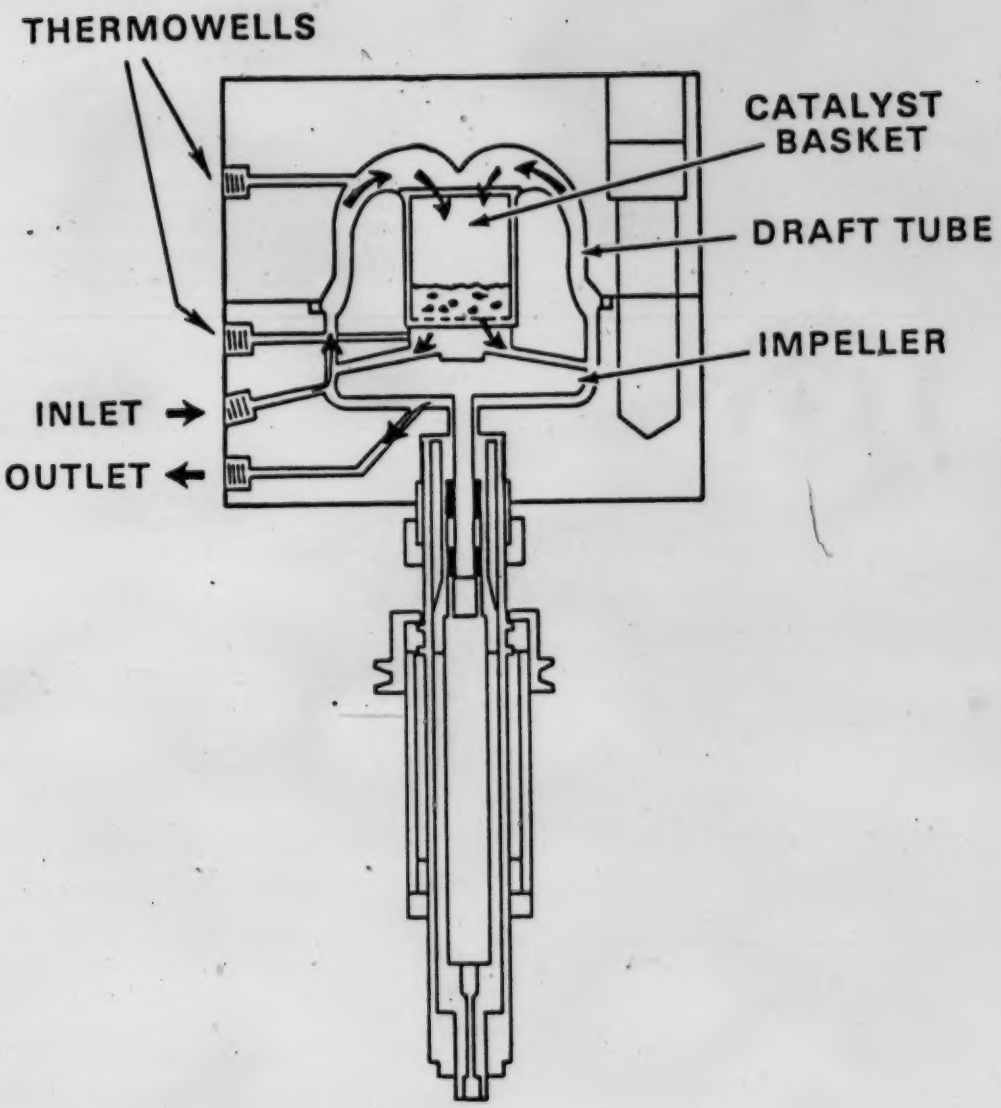


Figure 3.2 Autoclave Berty Reactor

$$Q = r\rho\,\Delta H = h\,a\,\Delta T$$

$$N = r\rho\nu = k\,a\,\Delta X$$

From these, it is possible to calculate ΔX and ΔT directly.

Using the data obtained from the oxidation of CO reactor study, empirical equations were derived to estimate the change in temperature and conversion across the catalyst bed for any set of reaction conditions.

The Reynolds number is defined as being,

$$Re = (79.9 * 10^{-6})\,(M\,P/T)\,(rpm/1500)(4\,Dp/L)^{1/2}/(a\,\psi\,\mu) \qquad \ldots\ldots (3.1)$$

for $Re < 50$,

$$\Delta T = 112\,r\rho\,\Delta H\,Pr^{0.66}\,(T/M\,P)^{0.5}\,(1500/rpm)^{0.5}\,(4/(L/Dp)^{0.25}\,/\,[Cp\,(a\,\psi)^{1.5}\,(\mu)^{0.5}] \qquad \ldots\ldots (3.2)$$

$$\Delta X = 47000\,r\rho\,\nu\,(T/P)^{1.16}/\,[(a\,\psi)^{1.5}\,(Dim)^{0.67}\,(M/\mu)^{0.16}\,(rpm/1500)^{0.5}\,(4\,Dp/L)^{0.25}] \qquad \ldots\ldots (3.3)$$

The full calculation and the definitions of the variables are given in the Appendix 2 and the nomenclature. For this work, the Reynolds number in the reactor is about 20. This results in a conversion of 0.05% across the bed and a temperature difference of 0.02 K. Thus these calculations support the assumption in this work of gradientless operation on the Berty reactor.

3.7.1 Autoclave Berty Reactor Description

The reactor is shown in Figure 3.2. The entire reactor portion was constructed of 316 stainless steel including the gasket which sealed the reactor vessel. The impeller was driven by a Magnedrive drive shaft which operates by a magnetic coupling, thus sealing the reactor from the main drive.

Heat to the reactor was supplied by three separate heating elements. These were fitted inside a heating jacket which slipped over the reactor housing. The two main

heaters, each rated at 2000 watts, covered the outer wall while the third, rated at 1000 watts, covered the top. The two main heaters were linked in series and supplied by a 208 volt supply. The top heater was connected to a 110 volt supply. The main heaters were controlled using a Foxboro controller, whereas the top heater was controlled using a Variac.

The design had several safety features. A high temperature cut-out was used to protect the heaters from overheating. This was set to 500 °C. The Magnedrive shaft was protected from the hot reactor by a water jacket. The water flow rate was monitored by a conductivity switch which would cut the heater power should the flow cease. The reactor temperature was monitored with Chromel-Alumel thermocouples. Lastly, iron-constantan thermocouples were inserted between the oven casing and the reactor wall to act as the sensors for the controller.

3.7.1.1 Reactor Operation

1. The reactor screws were tightened to 175 ft-lb, using a torque wrench applied in increments of 25 ft-lb cross-rotationally.
2. The reaction temperature was reached, starting from a cold reactor, after about six hours. The reactor was kept hot over a period of several runs.
3. All runs were carried out at 1200 rpm and the tachometer was found to be accurate. This instrument was checked using a stroboscope.
4. Cooling to room temperature took about three to four hours.

C100 anti-galling lubricant was applied to the screws at each dismantling. This was carefully cleaned off each time and no problems were encountered with seized screws.

Throughout this work, the reactor performed without any trouble, except towards the end when it was discovered that sulphur had back diffused past the top bearing and condensed on the shaft. The added friction caused the magnetic coupling to slip. The amount of sulphur was very small, however, in comparison to the length of time the reactor had been in operation and it was extremely unlikely that it had an effect on the experimental data.

3.8 Sulphur Condenser

The sulphur condenser used in this work was that designed by Liu (52), with some modification to adapt it to high sulphur flows. The main addition was a sulphur reservoir. This collected all the sulphur that condensed and had sufficient capacity to require only infrequent emptying. This vessel was added because it was found that liquid sulphur would plug the line leading to the top of the apparatus. This would cause pressure fluctuations eventually leading to excessive entrainment and plugging of the downstream system.

3.8.1 Operation

The sulphur condenser's performance was satisfactory considering that it was found impossible to remove all the sulphur in one condenser even at 115 °C (just above the melting point of 113 °C). It is likely that this was due to the formation of sulphur mist, a problem in industrial plants (91).

Approximately every two to three sulphur syringe fillings, the reservoir was removed, and emptied with the aid of a propane torch. It was found that vibration from the circulation fan motor tended to loosen some of the Swagelok fittings over a period of time and it was important to ensure that these were tight at the beginning of a series of runs in order to eliminate leaks.

3.9 Secondary Condensers

A small amount of sulphur was found to entrain from the main sulphur condenser. Therefore, it was necessary to make provision for this as it would rapidly plug the line at the first cold spot encountered. A system of three secondary condensers (15, 16, 17) was used to cope with this problem. This was operated in the following manner (the vessel numbers refer to Figure 3.1) :

1. Vessel 16 was unheated. It was packed with glass wool in the top section and with 5mm glass beads in the bottom. This effectively condensed the remaining sulphur and some of the water vapour, too.
2. Vessel 17 was required to condense the remaining water, otherwise it would

condense in the line to the control valve. Both vessels had valves so that the condensed water could be drawn off rapidly.

3. Vessel 15, in the GC sample line, was filled with 316 stainless steel turnings and served to remove the entrained sulphur in this line. This vessel and the line downstream were heated to approximately 80 °C to ensure that no water condensed before it reached the GC.

The line from the sulphur condenser to vessels 15 to 17 was maintained at a temperature similar to that of the sulphur condenser.

3.9.1 Operation

The main condensing system worked satisfactorily and the load on the secondary condensers was rarely too high. When it was, however, the entrance to vessel 15 became plugged. Usually, this was found to be due to the fact that the temperature of the main condenser had risen. The vessel flange could be removed and the plug eliminated by melting it, using a propane torch.

3.10 Gas Chromatograph

A Hewlett Packard 5700A gas chromatograph was used in conjunction with a Hewlett Packard 3700A integrator to perform the product analyses.

The product stream with the sulphur component removed was sampled manually for 12 seconds. The sample was passed through a five foot Chromosorb 108 1/8th inch column, using Helium at a flow rate of 35 ml/min. The column oven temperature was 90 °C. A thermal conductivity detector (TCD) analysed the sample composition. The temperature of the TCD was 115 °C and the current 160 mA.

Figure 3.3 Sample Chromatogram.

Column Chromosorb 108 1/8 in. by 5 ft.

Oven Temperature : 90°C.

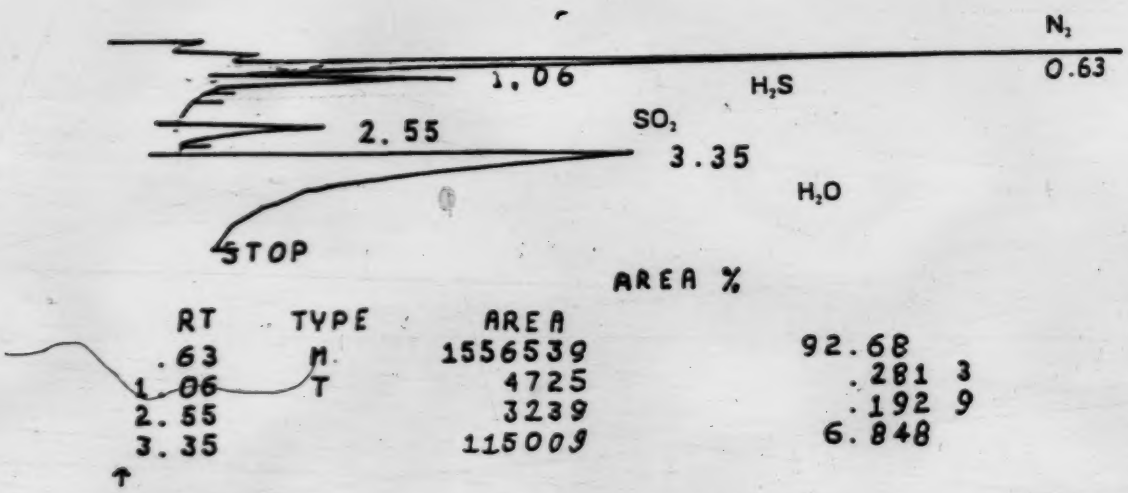
T.C.D. Temperature : 115 °C.

Detector current : 160 mA.

Carrier flow rate : 35 ml/min (He).

Chart Speed : 0.5 cm/min

Chart Attenuation : Logarithmic, 4 decades



The G.C. was calibrated several times throughout the course of the experimental programme in order to ensure that the response factors remained constant. The overheating of the column oven required the replacement of the columns and the TCD filaments. The new columns and operating conditions altered the response factors slightly. Otherwise, the response factors remained constant. The calibration procedure and results are reported in Appendix 1.

A sample chromatogram is shown below in Figure 3.3. Sample analysis, at a sensitivity of 0.03 mV/min, and allowing for the slight tailing of the water peak, took between five and eight minutes depending on the water concentration. On the average, ten samplings per hour could be made.

Previous studies performed by Liu (53) and Cho (15) had determined that a column consisting of Chromosorb 104 (4ft) and Poropak Q-S would satisfactorily separate the Claus reaction components. A column of this type was used initially, however, Chromosorb 108 gave a better separation and was adopted instead. The tailing of the water peak was less and the elution time shorter. This advantage may have been due to the low concentrations of H_2S and SO_2 involved.

3.11 Process Measurements

3.11.1 Pressure

1. Atmospheric : measured by a Fischer mercury barometer in the neighbouring laboratory, reading in mmHg.
2. Nitrogen : measured using a USG gauge, calibrated at 8.5 psig, reading accurate to 0.1 psig.
3. Reactor : measured just upstream of the sulphur mixing, using a Dynisco pressure transducer PT25-30 and a Foxboro chart recorder.

3.11.2 Temperature

1. Feed : sensed by an Iron–Constantan thermocouple.
2. Reactor : sensed by a Chromel–Alumel thermocouple.

All thermocouples were connected to a Honeywell 24 point chart recorder calibrated to read 0–30 mV. The reference temperature was 0 °C, using an ice–water bath.

3.11.3 Flow Rates

1. Nitrogen : Volumetric flow rate measured by a differential pressure cell.
2. Water : Mass flow rate obtained from the syringe pump calibration.
3. Sulphur : Mass flow rate obtained from the syringe pump calibration.

3.11.4 Process Control

1. Nitrogen flow : Moore differential flow controller.
2. Reactor pressure : Foxboro controller.
3. Reactor temperature: Foxboro controller.

3.12 Calibrations

1. Pressure Transducer

$$\text{cm Hg} = 0.89557 * R\% + 0.01379$$

where R is the chart reading.

2. D/P Cell

$$Q^2\ (\text{l/min})^2 = 0.089984 * R\% - 0.053501$$

3. Thermocouples

Feed : Accurate to within recorder reading, ±0.15 mV.

Reactor : Accurate to within recorder reading, ±0.15 mV.

4. Water Syringe Pump

Range 0.01:– $G\ (\text{g/min}) = 4.66522 * 10^{-4} * R\% - 9.3262 * 10^{-3}$

Range 0.001:– $G\ (\text{g/min}) = 4.56200 * 10^{-5} * R\% - 1.0665 * 10^{-4}$

5. Sulphur Syringe Pump

Gear		g-atoms S_1/min
L1	=	$4.686 * 10^{-2}$
H1	=	$7.376 * 10^{-2}$
L2	=	$9.979 * 10^{-2}$
H2	=	$1.4817 * 10^{-1}$
L3	=	$1.9420 * 10^{-1}$
H3	=	$3.0729 * 10^{-1}$

6. G.C. Response Factors

$H_2O = 0.8747 + 0.01918 * mol\% - 0.00091 * (mol\%)^2$

$H_2S = 1.841969$

$SO_2 = 1.2077$

3.13 Materials

Specifications supplied by the manufacturers.

Nitrogen : Linde Gas products High Purity 99.99% . . . . . O_2 main impurity

Sulphur : Fisher nf grade sublimated . . . . . H_2O main impurity

Water : Triple distilled (24) 99.99% . . . . . N_2 main impurity

Catalyst : Kaiser S201 alumina

area 380 m^2/g

chemical composition,

SiO_2 0.02%

Fe_2O_3 0.02%

TiO_2 0.002%

Na_2O_3 0.3%

Al_2O_3 93.6%

loss on ignition 6.0%

size, 8-9 mesh, 2.00-2.38 mm

3.14 Alternative Equipment

Over the course of this study, several forms of equipment were either modified or discarded. The reactor used in the preliminary stages of this work and the reasons for discarding it have been discussed. This was replaced mainly because it required frequent maintenance. The original gas chromatograph, a Microtek 2003, was replaced with a Hewlett Packard 5700 for the same reason. The recorder baseline often became noisy. This problem was attributed to an indetectable air leak and was not encountered with the Hewlett Packard gas chromatograph.

The main disadvantage of the experimental system was the irregularity that was observed in the water feed when both the sulphur and water pumps were operating. Two approaches could be taken in the attempt to solve this problem.

1. Sulphur Feeder

Since the syringe pump itself appeared to operate smoothly, the root of the problem was likely to be the successive drops of sulphur evaporating irregularly in the sulphur mixing vessel. The surge vessel was inserted to smooth the flow. This vessel's capacity was large enough to accommodate the flow between one sulphur drop and the next. No difference in the flow characteristics was observed between high and low flows of sulphur and so it was unlikely that an even larger vessel would have eased the problem.

The replacement of the pump itself with a sulphur saturation system was considered. Many operational problems were anticipated, however, and the use of such a system would have required the entire rebuilding of the reactor feed system. It was decided to continue with the syringe pump in order to determine whether sufficiently precise data could be obtained with the original equipment.

2. Water Feed

It was possible that the feed fluctuation was due to the actual variation in the water flow itself. It would have been possible to eliminate this using a water saturator. Since this equipment would have been considerably easier to build and test than the sulphur saturator, preliminary tests were made employing a water

saturator without the equipment required for the fine metering of the flow. This apparatus consisted of two water spargers in series, immersed in a thermostatically controlled water bath.

Unfortunately, several problems were encountered. The system had a high pressure drop which restricted the flow rates that could be obtained with the normal pressure available from a standard nitrogen cylinder (60 to 70 psig). The fixed sulphur flow rates meant that the water flow had to be easily adjustable. This was especially desirable in view of the amount of data required in an experimental initial rate study. The main reason, however, that the saturation system was discarded was the fact that the scale deposited in the sulphur mixing vessels proved to be catalytic, and it was necessary to add the water feed just before the feed stream entered the reactor. In order to allow a sulphur saturation to operate, two streams, one of water/nitrogen, and the other of sulphur/nitrogen, would have to be blended. By careful control of the compositions of each stream and the ratio of their flow rates, the required feed stream composition could be achieved. A much more complex feed system would therefore have been required in order to improve on the one used in this work.

To summarise, it is likely that the above problems could be solved, but that a very much more complicated and expensive feed system would be necessary. This would probably involve the use of water and sulphur saturators, and include the use of two separate feed streams, S/N_2 and H_2O/N_2. Each of these streams would require on-line analysis and precise flow measurement and control. A sulphur saturation system would require precise control of high temperatures, 300 - 400 °C, and of nitrogen flow rates, in order that the particular feed flows required could be quickly and reliably obtained.

4. EXPERIMENTAL PROGRAMME

4.1 Introduction

The Claus reaction is a reversible reaction with the equilibrium favouring the reverse reaction, that is, the production of sulphur and water. With such a reaction, it is necessary to consider both the forward and the reverse components in any kinetic analysis. This requirement necessarily doubles the number of parameters to be determined by the data reduction. It is advantageous, therefore, to simplify the rate equation by considering the special case of the initial rates. This will set the product term in the overall rate equation at zero, in which case the reaction may be regarded as a single, irreversible one. For example, for the general gas phase reaction ,

$$A + B \rightleftharpoons C + D \qquad (4.1)$$

the general rate equation is of the form

$$-Ra = k_1 Pa\, Pb - k_2 Pc\, Pd \qquad (4.2)$$

In the initial rate case, the last term $\longrightarrow 0$,

$$-R(\text{initial rate}) = k_1 Pa\, Pb \qquad (4.3)$$

The number of experiments required to collect initial rate data is far greater than that required for irreversible reaction studies, since a series of finite rate data points are required to obtain one initial rate datum. The initial rate method, however, reduces considerably the total number of parameters that must be estimated from the data. This allows the data to be used to obtain more specific information on the reaction rate. Also, the data is not wasted since, once the forward and reverse terms have been determined, all the data collected may be used to estimate the form of the overall rate equation. The present study does not include such an analysis of all the data.

McGregor (56) used the initial rate method to investigate the forward Claus reaction. He followed the data analysis suggested by Mezaki and Kittrell (59). This work will adopt that same approach. Essentially, the following argument is applied (48) :

The mass balance for a CSTR yields ;

$$-R = Fa\ Xa/Wt \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

Rearranging this we obtain ;

$$Xa = -R\ Wt/Fa \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.5)$$

A plot of Xa versus Wt/Fa will yield a smooth curve, the slope of which, at a given conversion and reciprocal mole flow rate, is equal to the rate of reaction. However, this rate of reaction is not the overall rate of reaction since the molar feed rate to the catalyst bed is not the same as the molar feed rate to the reactor. In the limit, as Wt/Fa --> 0, Fa --> infinity , the mole feed to the bed and the reactor are almost identical. As a result, the slope of this curve at the origin, that is, zero conversion, will be equal to the initial rate of reaction.

The slope at the origin may be derived from the experimental data by fitting the points with some smooth curve that passes through the origin by using a least squares parameter estimating technique. Mezaki and Kittrell (59) suggested using the nonlinear curve,

$$Y = A \tanh(B\ X)$$

where X is the independent variable and Y the dependent variable. A and B are parameters which must be determined by a least squares analysis. This curve has the advantage that its derivative at the origin, which is equal to (A*B) , may be calculated analytically (Appendix 3). Thus, the initial rates may be obtained quickly from a non-linear least squares fit of this function to the data. A series of conversion vs. (mole flow rate) $^{-1}$ curves will therefore yield the initial rate vs. partial pressure data required to perform an empirical study of the reverse reaction.

Once the orders of the reaction have been ascertained, the rate constant of the reaction can be calculated. By conducting initial rate runs at different temperatures, it is possible to determine the apparent activation energy and the temperature dependence of the rate constant by a plot of log(k) vs. 1/T (48).

4.2 Preliminary Experiments

Several preliminary experiments were necessary to ensure that the rate data obtained were reliable.

4.2.1 System Inertness

Initially, and at several times throughout the experimental study, the reactor equipment was tested for catalytic activity. This was done simply by feeding the reactants into an empty reactor and testing for reaction products. The spinning basket reactor system originally used (82) was found to be catalysing the reaction. By careful cleaning of the equipment, the reaction products, attributable to residual carbon dust in the reactor, were reduced to a negligible amount. Though the Autoclave reactor was found to be unreactive at the beginning of its use, after a period of time reaction was discovered to be taking place in the sulphur mixing section. This was attributed to a carbonaceous deposit which was found to have coated the inside surface of the mixing vessel. It is believed that this material originated in the sulphur syringe itself, possibly from the teflon "O"-rings, and possibly from the valve packings. The valves themselves had to be replaced on two occasions because they leaked. Complete cleaning of the interior of the sulphur mixing vessels proved to be impossible, so they were replaced. The problem was effectively eliminated by placing the water feed just before the reactor. The deposit was effectively trapped by the mixing vessels and there was no further problem with extraneous reaction. Unfortunately, however, this arrangement precluded the use of water saturators for the water feed.

Particular attention was paid to the possibility of reaction within the sulphur condenser. Karren (39) had reported that liquid sulphur catalysed the reaction. The tests for system inertness were carried out with the full experimental system which included the sulphur condenser. Since liquid sulphur was present in the condenser and no hydrogen sulphide or sulphur dioxide were detected, it was concluded that liquid sulphur did not catalyse the reaction.

4.2.2 Ideal Mixing and Bulk Diffusion

All reactors of the CSTR configuration must be evaluated to ensure that the basic assumption of ideal mixing is valid. The Berty reactor can easily be tested by running the reactor at constant feed composition and varying the impeller speed. Above a certain impeller speed, the conversion will remain constant, indicating that the mass velocity of the reactants across the catalyst bed is no longer influencing the reaction rate. Figure 4.1 shows a plot of conversion versus impeller speed. This shows a regime in which the impeller speed has no effect on the conversion. As the figure indicates, ideal mixing is achieved at impeller speeds of greater than 1000 rpm.

The feed conditions used in this test were more severe than those used in the kinetic runs. A higher space velocity and catalyst loading ensured that the actual kinetic experiments would be carried out under ideal mixing conditions. An impeller speed of 1200 rpm was therefore chosen for all runs.

The impeller speed experiment also determined that neither interphase, nor bulk diffusion effects, were rate limiting.

(A similar experiment with the Turner spinning basket reactor determined that much higher speeds were required to ensure ideal conditions pertained inside the reactor vessel because of the small diameter of the impeller.)

4.2.3 Catalyst Activity

It is essential in any heterogeneous catalytic study that the catalyst activity remain constant over the period of the experiments, otherwise it becomes an additional variable, one which is difficult to quantify. The analysis of the deactivation of catalysts is a specialised field of study. In this study, Kaiser S201 alumina catalyst was used. This is reported to be a very robust catalyst (67) which maintains its activity over long periods of time.

It was found that the apparent activity of the catalyst in the Turner spinning basket reactor system increased with time. This was attributed to carbon dust rather than to any real increase in activity.

With the Autoclave reactor, the activity of the catalyst was found to remain constant over the period of the experimentation.

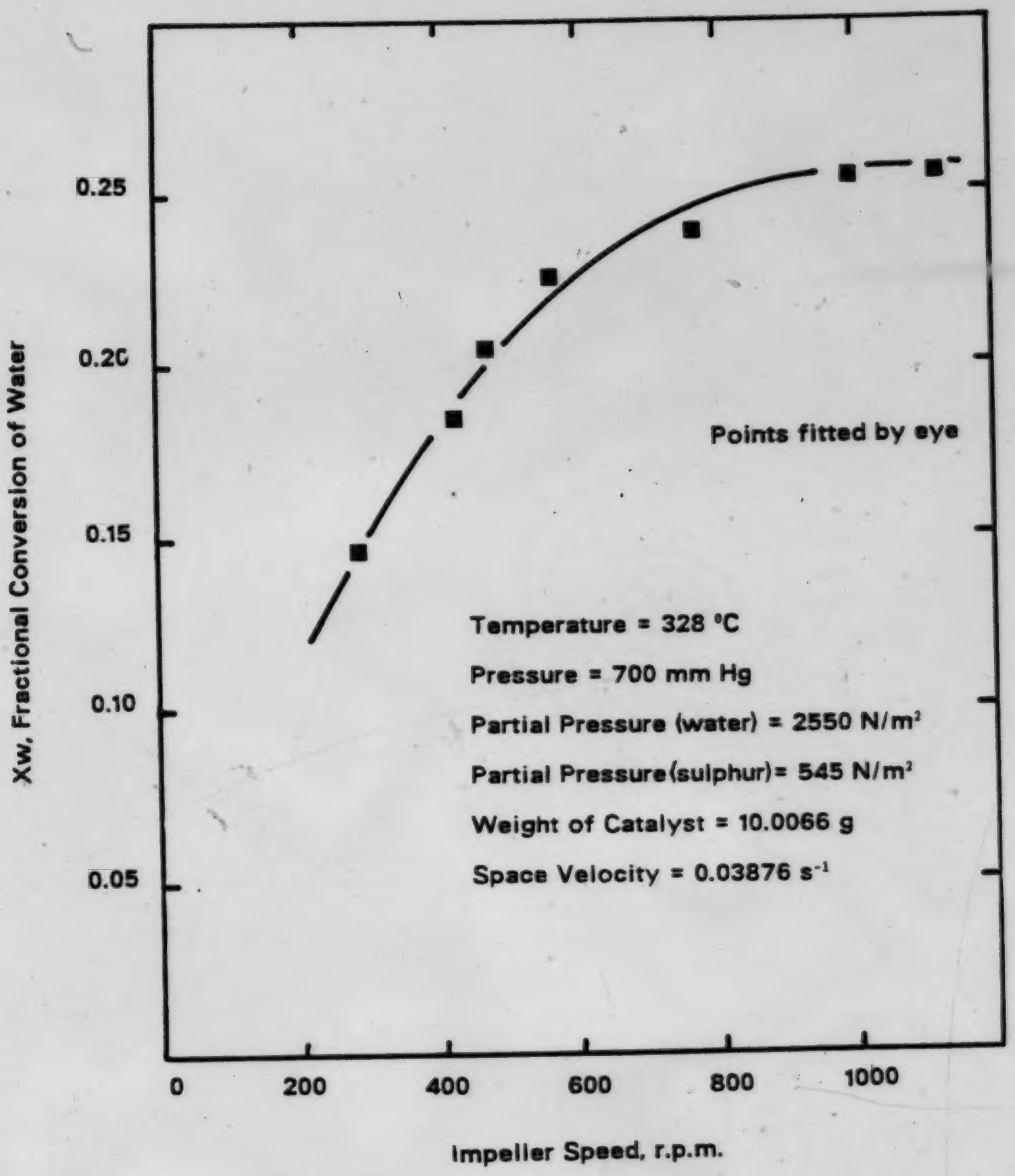


Figure 4.1 Conversion versus Impeller Speed

4.2.4 Volume of the Reactor

The volume of the reactor was measured in the following way. For an ideal gas at constant temperature, P V = constant. From this relation, the volume of a vessel may be calculated. The theoretical analysis is given in Appendix .1.

Figure A-1.2 in the appendix illustrates the apparatus used to determine the reactor volume. A cylinder of known volume (500 in^3) was filled to about 70 psig and connected via a valve to the reactor. Atmospheric pressure was recorded and the valve was opened slowly to allow the gas to expand into the reactor ideally. This procedure was repeated six times and the volume of the reactor was calculated each time. The actual reactor volume was taken as the average.

4.2.5 Repeatability of G.C. Peak Areas

The accuracy of any reaction study is limited by the reliability of the product sampling techniques. It was found that the water syringe feed gave a constant water flow rate as shown by the G.C. water peak area. For example, for one particular flow rate,

$$\text{Average } H_2O \text{ Peak Area \%} = 1.920 \pm 0.0590 \ (3.07\%)$$

The syringe was calibrated for the entire range of flows to be encountered, and the actual water composition in the stream was known. It was this method that was used to calibrate the G.C. water peak. The introduction of the sulphur feed, however, caused the water peak to fluctuate by as much as 10%. As a consequence, it was decided to calculate the water feed concentration directly from the products using the hydrogen sulphide peak in order to establish the actual water feed.

From the product analysis, the molar flows of H_2S and H_2O were calculated. From the reaction mass balance, the molar flow rate of water in the feed stream must be equal to the sum of the H_2S and H_2O product flows.

This approach was necessary since the introduction of the sulphur feed affected the water feed rate and as a result the actual water feed flow was unknown. The material balance across the reactor can now be checked by the g-atom balances on

oxygen and sulphur only.

An important consequence of using this method is that the observable error associated with the product analysis is distributed between the calculation of the water feed and the product, rather than being concentrated in the product analysis. This will be discussed more fully in the discussion section 5.8.

4.2.6 Ideal Gas Law

In the material balance calculations used in deriving the rate data in this study, the ideal gas law has been assumed to be valid. This assumption is shown to be valid by calculation of the component fugacities, (Lewis (50)). Pure component fugacity coefficients may be estimated using generalised compressibility charts and the principle of corresponding states. The critical constants and the reaction system are shown below. The fugacity coefficients are estimated from the generalised property charts of Newton (64). It is apparent that, at the temperature and pressure of the reactor, the fugacity coefficients are very close to unity. Though the charts are not precise at such low reduced pressures, the error is but a few percent. At room temperatures, McGregor (56) indicates the gases may all be treated as ideal. Sulphur is not part of the material balance at room temperature.

Table 4.1 Critical Constants and Fugacity Coefficients.

Species	Tc (K)	Pc (atm)	Zc	Pr (1.46atm)	Tr (600K)	γ
N_2	126.0	33.5	0.291	0.0436	4.76	1.0
H_2S	373.6	88.9	0.284	0.0164	1.606	1.0
SO_2	430.7	77.8	0.269	0.0188	1.393	1.0
H_2O	647.4	218.3	0.230	0.0067	0.927	1.0
S	1313	179.7	0.2	0.0081	0.457	0.98

The critical property data were obtained from JANAF (36) thermochemical tables for all species except sulphur whose properties were obtained from Rau et al.(71).

4.2.7 Sulphur Vapour Equilibrium

It has been assumed in this study that the sulphur vapour has sufficient time to reach an equilibrium distribution of species. Although data is available on the equilibria of the various sulphur species, none is available on the rates of these reactions. Berkowitz (4) considers these rates briefly. He reports that there is evidence that the rate of equilibration of the sulphur species is slow. He suggests that the activation energy of the equilibration is probably related to the strength of the sulphur–sulphur bond in the ring. A large surface area is reported as being an aid in achieving equilibrium sulphur vapour. The nature of that surface was also a factor. Qualitative experiments to determine the rate of equilibration were made over the range of 300–350 K.

The temperature and design of the sulphur mixing system were such that they would tend to improve the rate of equilibration. The sulphur mixing vessel was tilted at an angle of approximately 25° from the vertical. This would ensure that the liquid sulphur droplets would fall directly onto the vessel wall providing a large surface area for evaporation. The sulphur inlet line was 1/16 inch stainless steel tubing which projected 1 inch into the vessel and which had been filed to resemble a syringe needle. This arrangement ensured that the incoming sulphur contacted the nitrogen flow directly and the needle itself provided as large an area as possible for evaporation. A surge tank was also added to increase the time available for the mixture to equilibrate. There is no simple test, however, to determine whether the assumption that the sulphur vapour equilibrium is attained is a reasonable one.

4.2.8 Intra-phase Pore Diffusion

Diffusional resistances within the catalyst pellet may be rate–limiting (10, 48, 73). These effects depend on the relative rates of diffusion and on the surface reaction. The single pore model, as analysed by Levenspiel(48), shows that the rate of reaction will be diffusion–limited if $(L\ k/D) < 0.5$. Thus, for small L, pore length (that is, small catalyst pellet), slow reaction rate, and high diffusion, it is less likely that pore diffusion will be rate–limiting.

It is possible, then, to test whether such an effect is present by a series of experiments measuring the conversion versus catalyst pellet size. McGregor (56)

performed this test with two catalyst sizes, 0.6 mm and 0.25 mm. The rate of reaction was much higher with the smaller catalyst pellet. McGregor concluded that the rate was proportional to the external surface area of the catalyst. George (30) and Landau et al. (47) determined that, with pellet diameters of over 2 mm, all the rate function parameters, except the rate constant, remained constant. Liu (53) analysed his i.r. studies of the Claus reaction using criteria suggested by Hudgin (89) and also by estimating the effectiveness factor. He used catalyst wafers 2 mm thick. He concluded that pore diffusion was insignificant in his studies.

No test for pore diffusion effects was made in this study. McGregor's conclusion that the reaction rate was proportional to the external area of the catalyst is assumed to be valid in this study. The catalyst size used in McGregor's work was 0.6 mm as compared to 2 mm in this study. The reaction rate, however, is much less -- by a factor of ten , (see Appendix 2) - so that the possibility of rate-limiting pore diffusion is much less. The possible effect of significant pore diffusion resistance in the light of the data obtained in this work will be examined in the discussion section, 5.8.

4.3 Kinetic Experiments

The reverse Claus reaction is a function of the partial pressures of water and sulphur, and of temperature. Since it was expected from the results of previous studies on the forward reaction (30,53,56) that water adsorption would inhibit the reaction, the easiest parameter to isolate and evaluate was that of the order of the reaction with respect to sulphur, since in that case the water partial pressure is kept constant as is the reaction temperature. Having established the sulphur order of reaction, the dependence of the reaction on the partial pressure of water can be investigated with a view to establishing whether or not water does indeed inhibit the reaction, and whether an adsorption term in the rate expression can satisfactorily explain this inhibition. Additional runs at higher temperatures may then be made in order to investigate the temperature dependence of the reaction.

4.4 Experimental Procedure

4.4.1 Start-up

Initially, the entire system was flushed with nitrogen. The temperatures of the various sections were adjusted when necessary. The entire system including the preheat oven, sulphur condenser, et cetera, took about ten hours, when starting from room temperature, to come up to operating temperature. About one hour before running, the flow rate of nitrogen was set to that required for the experimental runs in order to allow the temperatures to equilibrate.

The flow rates of N_2 and H_2O were determined by the particular sulphur syringe gear that was engaged. The settings that were required to obtain these flow rates were calculated from the calibration equations for the D/P cell and the water syringe pump respectively.

Once the temperatures and pressures were as required, the water feed and reactor fan were started. It was important to check at this stage that the system was functioning as expected, since it was possible that the water feed line had become blocked. The gas chromatograph was used to check that the required partial pressure of water was being achieved.

Once the system had come to reasonable steady state, as determined by the temperatures, flow rates and G.C. analysis, the sulphur flow was started. The appropriate gear having been engaged, the sulphur feed valve was opened. Unfortunately, the only indication of sulphur flow was the appearance of reaction products in the effluent stream. When starting from a sulphur-free system, it would be one to two hours before the sulphur feed was fully established and steady state attained.

The required feed rates having been attained, quantitative analysis of the product stream was possible. The reaction products were monitored over a period of about an hour in order to establish the true steady state reaction. The general procedure was to obtain six analyses at the steady state which might then be averaged.

4.4.2 Running

Once the system was operational, the steady state could be altered quite rapidly by adjusting the feed rates of the reactants. The reactor returned to steady state within 15 minutes of its being changed. In this manner, several runs could be made in one day.

It was important that the temperatures and pressures of the system be monitored regularly to ensure that any problems, especially plugging by sulphur, were detected quickly.

4.4.3 Shutdown

After a series of runs were completed, the system was shut down. It was important that this be done carefully to avoid sulphur condensing anywhere other than inside the sulphur condensers. This was achieved by immediately shutting off the sulphur feed and closing the sulphur feed valve, thus isolating the syringe from the main system. The relative amount of sulphur passing through the reactor could be estimated by a continuation of the monitoring of the product stream with the G.C. On average, it took about 60 minutes for the amount of reaction products to become negliglible. At this point, the water feed was stopped. Full nitrogen flow was maintained for another 30 to 60 minutes and then was reduced to a few cc's per minute. The drain valves of the final condensers were opened at this point to drain off the collected water and also to ensure that the low flow nitrogen had free passage.

The entire system was left at the operating temperature overnight so that the next set of runs could be begun quickly. This was also found to be extremely useful as an extra precaution against the condensation of any residual sulphur in the lines.

4.4.4 Maintenance

The principal maintenance of the reactor system involved the periodic cleaning of the sulphur condenser. The condenser was not arranged so that this could be performed on-line. Though on-line cleaning would have been an advantage, the modification described in the equipment section considerably increased the period between drainings, and therefore decreased the need for cleaning.

The build up of scale inside the sulphur mixing vessels was the only other serious problem. This was bypassed by placing the water feed just before the reactor.

4.5 Data Reduction

Most of the experimental measurements of temperatures, pressures, and flow rates, were obtained in terms of a percentage of full scale readings on an electronic recorder. The rest were obtained by a variety of other means. Atmospheric pressure, for example, was read from a barometer in mm Hg. Feed water flow rates were obtained from the calibration equation of the syringe pump (see Appendix 1) and also from the reaction mass balance. Nitrogen feed pressure was read in psig directly. The reactor and feed temperatures were converted from the mV readings obtained from the temperature recorder, to degrees Celsius using the thermocouple tables from the CRC handbook (14) and the calibration factor. The pressure data were converted to absolute pressures in atmospheres according to the calibration equations as derived in Appendix 1 The nitrogen flow rate was converted to litres per minute by means of the calibration equation as shown in Appendix 1.

The product compositions were calculated from the gas chromatograph peak areas for each component as shown in Appendix 2. These gave a mole per cent on a sulphur free basis. The actual mole percentages were obtained using the mass balances. The ideal gas law was applied to all species and the nitrogen gas stream served as a basis for calculation since this component was inert and the same amount comprised the feed and the product streams. From the calculated nitrogen flow and the product compositions, the molar flow rate of each of the products was obtained.

The equilibrium distribution of the sulphur species was estimated by using the Gibbs free energy minimisation method and by assuming that only the sulphur species S_2, S_4, S_6, and S_8 were present in the vapour. It is known that this is only an approximate method of estimating the sulphur species distribution (72) but these species were chosen with the view that the free energy data on them are the most reliable available .

The fractional conversion was obtained from the difference in the molar flow rates of each of the reactants.

The partial pressures of all species were calculated using the calculated sulphur species distribution, and assuming these species to be in equilibrium with each other, the mole fractions of the other species, and the total pressure.

A computer program for carrying out these calculations, including the processing of the raw data and the reactor material balance, is shown in Appendix 3. A listing of this program, a flow chart describing its operation, and a detailed calculation of one set of raw data is given.

4.5.1 Initial Rate Calculation

In order to obtain initial rate data, it was necessary to plot conversion versus the inverse molar flow rate and obtain the slope of the resulting curve at the origin. This was done by fitting the curve $Y = A \tanh (B X)$ by means of a non-linear curve fitting technique. The method used was that of Meyer and Roth (58) and it proved extremely effective in the calculation of a least squares estimate of the parameters of the Tanh function, provided that the experimental data had been scaled to ensure that the exponentials were small. The initial rate is given by the derivative of the function at the origin. This function may be differentiated analytically as shown in the Appendix. Thus, the initial rate is obtained by multiplying the non-linear least squares estimates of the parameters A and B. Appendix 3 lists the program used to fit this data.

5. RESULTS

5.1 Introduction

A total of 173 finite rate experiments were performed. Of these, 113 were performed at a constant temperature and water partial pressure. From this data, the initial rate of reaction is derived for 10 sulphur partial pressures. In addition, the equilibrium conversion is estimated for 6 different sulphur partial pressures. Of the remaining runs, 50 were carried out at constant sulphur partial pressure and a further 8 initial rates were obtained. An additional 10 runs were performed at two higher temperatures, yielding another two initial rates.

Each individual run is identified by a five character name, viz.

SI04A, – Sulphur Initial rate data set,

ie. sulphur partial pressure varying.

04, 10 * nominal total sulphur percentage in feed (0.4%).

A, individual run identifier

hence,

WI01A – Water Initial rate data set,

ie. water partial pressure varying.

01, nominal percentage of water in the feed (1%).

A, individual run identifier.

and,

WT6HA – Water Temperature run,

ie. initial rate with high water partial pressure and higher temperatures for the series of runs.

6, nominal percentage of water in the feed, (6%)

A, individual run identifier.

A total of 53 runs were made at low space velocities during the development of the reactor system. These determined the experimental conditions required to obtain repeatable data and also provided a series of data sets from which it is possible to

estimate the equilibrium conversions.

Prior to reducing the quantity of catalyst employed in order to allow the taking of initial rate data, the G.C. oven ran "wild". Inexplicably, the oven heater was suddenly given full current, and the temperature rapidly increased, baking the column and fouling the thermal conductivity detector filaments. The column and the filaments were replaced and the G.C. recalibrated. The problem recurred on two occasions, however a lead thermal fuse was used to protect the column from overheating and there was only a short interruption in obtaining the experimental data. As a result of this problem, all the experimental runs used to obtain the initial rate data were performed after the G.C. had been re-calibrated, from October 1980 on. Runs conducted prior to this date were not used in the initial rate analysis but were used to determine the equilibrium conversion. The G.C. calibration for these preliminary runs is therefore slightly different.

Appendix 3 contains both the computer programs and sample outputs that were used to calculate the values of the kinetic parameters of the reaction. The computer program EXPTCAL was used to analyse the raw data obtained from each run. A sample of the main output from this program is given after the program listing. A summary of each and every run that was performed is contained in Appendix 4. The program REGRSS was used to analyse the conversion/space time experimental data. The subroutine NLSYST established the non-linear least squares fit to the data. The output from this program illustrates the experimental data points and the least squares estimated points. This output is contained in Appendix 4. The program IRANAL was used to calculate the least squares estimate of the parameters of the function which it had been suggested would describe the water dependency of the reaction (equation 1.1). The output from each of the various estimates of these parameters is given in Appendix 4.

5.1.1 Sulphur Dependence

Initial rate experiments were performed to determine the order of the reverse Claus reaction with respect to sulphur. These were performed at a constant pressure, temperature, and partial pressure of water. The partial pressure of sulphur was varied over the entire range that the experimental system would permit. The mole fraction of sulphur(8) ranged from 0.14 - 2.0%, corresponding to a partial pressure of

266 – 3000 Pa. The partial pressure of water was held constant at about 2.5%, ie. 3700 Pa. The temperature was 592 K and the pressure, 1.46 atmospheres. A total of 55 runs were made at 10 different partial pressures of sulphur yielding 10 initial rates. At least 3 runs were made for each set of conditions at molar feed flow rates as high as possible in order to obtain data near to zero conversion.

5.1.2 Water Dependence

The water dependence of the reaction was analysed by performing initial rate experiments at a constant sulphur partial pressure of 753 Pa. The temperature and pressure were equal to that used in the sulphur experiments, that is 592K and 1.46 atm respectively. The mole fraction of water used varied from 1 to 14.5% and eight different partial pressures were employed. The partial pressure of S_8 was about 0.5% of the total pressure. A total of 50 runs were made over a range of inverse molar feed rates of 1 – 40 g hr/mol.

A minimum of 5 runs were made at each set of conditions. Five runs were possible since the water feed rate could be smoothly varied over a wide range. As with the SI experimental series, the highest molar feed rates possible were employed.

5.1.3 Temperature Dependence

Two additional initial rate data sets were carried out at temperatures above 592 K, namely 624 K and 653 K. Higher temperatures were chosen to avoid any problems that might have arisen by operating close to the sulphur dew point. At the partial pressures of sulphur employed, the sulphur dew point was around 550 K. The partial pressures of the reactants were kept close to that of the 592 K set of runs, WI06, although exact correspondence could not be achieved since the higher temperatures are expected to alter the sulphur species distribution. An additional 10 runs were performed which, combined with the WI06 data set, give the initial rate of reaction at three temperatures.

5.2 Analysis of SI data

A total of 62 runs were performed at a constant water partial pressure in order to establish the dependence of the reaction on the partial pressure of sulphur. These runs are summarised in Table 5.1 below. The full raw data are given in Appendix 4. The conversion and space time data calculated in the initial data analysis, are used to obtain the initial rate of reaction. Figure 5.1 illustrates this data for one data set SI04. The results of the non-linear curve fitting program REGRSS are contained in Appendix 4 and these show both the experimental data and the fitted data. The run SI25B was not used in the data analysis since the calculated conversion was much lower than that suggested by a smooth curve through the remaining points. An inspection of the raw data reveals that the pressure in the experimental system was much lower than usual for an experimental run. This would suggest for example, that a drain valve had been left open. This would reduce the molar feed rate of nitrogen and water increasing the relative amount of sulphur and as a result this run cannot be used for initial rate analysis.

Having obtained the initial rate data, the partial pressure of sulphur(8) may be plotted as a function of the rate of reaction to illustrate the relationship between the two. A simple plot of rate against partial pressure yields a curve. The form of the rate equation that is thought to pertain (equation 1.11) suggests that a log-log plot will show a straight line, the slope of which is the order of the reaction with respect to sulphur. The log-log plot (Figure 5.2) shows the data collected at various sulphur concentrations and indicates a straight line correspondence. This plot is used to derive the order of reaction with respect to sulphur by linear regression,

$$\text{order wrt } S_8 = 0.397 \pm 12\%$$

The limits of accuracy have been determined from the slope variance as shown in Section 5.6.1.

TABLE 5.1 DATA SETS SI (summary)

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
SI04P	1.4783	591.15	1.8063	0.1692	167.53	0.0903
SI04O	1.4736	591.15	2.1248	0.1723	213.74	0.1089
SI04N	1.4783	591.15	2.1514	0.1781	336.05	0.1343
SI04Q	1.4754	591.15	2.1921	0.1862	126.98	0.0876
SI04R	1.4757	591.15	2.0736	0.1786	80.914	0.0586
SI04S	1.4780	591.15	2.0490	0.1858	62.844	0.0463
Avgs	1.4767	591.2	2.0062	0.1784		
SI05H	1.4757	591.15	2.8147	0.2594	317.69	0.1341
SI05I	1.4809	592.15	3.1215	0.2435	204.43	0.1128
SI05J	1.4792	592.65	2.4115	0.2507	60.70	0.05416
SI05K	1.4792	593.15	2.4417	0.2194	79.51	0.06101
Avgs	1.4789	592.3	2.4235	0.2433		
SI06I	1.4839	592.15	2.7762	0.2896	119.84	0.0935
SI06K	1.4792	591.15	2.5320	0.2936	58.76	0.05022
SI06J	1.4816	591.15	2.8954	0.3057	74.81	0.07074
SI06L	1.4796	591.15	1.9773	0.3030	38.07	0.04059
Avgs	1.4813	591.4	2.5452	0.2980		

Table 5.1 continued.

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
SI08L	1.4608	593.15	2.0413	0.3939	469.54	0.0887
SI08M	1.4728	594.15	2.2316	0.3742	309.96	0.0999
SI08N	1.4683	593.15	2.0014	0.4072	235.43	0.0864
SI08O	1.4681	593.15	2.1379	0.4066	235.47	0.0876
SI08Q	1.4759	591.15	2.1380	0.4127	188.48	0.0874
SI08R	1.4771	591.15	2.1159	0.4014	147.80	0.0801
SI08S	1.4749	591.15	1.8771	0.3792	74.96	0.0544
SI08T	1.4820	591.15	2.0055	0.3809	96.91	0.0616
SI08U	1.4769	591.15	2.5693	0.4062	71.88	0.0573
SI08V	1.4792	591.15	2.4744	0.4145	56.01	0.0494
SI08W	1.4821	593.15	2.1059	0.4027	37.04	0.0401
Avgs	1.4755	592.0	2.1584	0.4013		
SI10K	1.4669	593.15	2.1451	0.6120	288.22	0.0708
SI10J	1.4680	593.15	2.1579	0.6048	443.66	0.0728
SI10L	1.4669	594.15	2.1586	0.6037	224.63	0.0696
SI10N	1.4751	593.15	2.0732	0.6141	144.25	0.0667
SI10M	1.4681	593.15	2.2994	0.6114	223.00	0.0762
SI10P	1.4749	591.15	2.1178	0.6287	70.12	0.05090
SI10Q	1.4820	591.15	1.9474	0.6056	45.60	0.04327
SI10O	1.4820	591.15	2.3135	0.6352	90.59	0.06182
SI10S	1.4793	591.15	2.8935	0.5741	53.65	0.05608
SI10R	1.4397	591.15	2.6130	0.6036	178.70	0.0697
SI10U	1.4596	594.65	2.2145	0.5737	27.51	0.03038
SI10T	1.4584	591.15	2.7753	0.5857	34.76	0.04138
Avgs	1.4680	592.0	2.3912	0.6008		

Table 5.1 continued.

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
SI15G	1.4669	593.15	2.3538	0.8776	275.42	0.0613
SI15H	1.4633	593.15	2.2116	0.8684	213.26	0.0574
SI15I	1.4751	593.15	2.2999	0.8456	138.53	0.0586
SI15J	1.4771	591.15	2.3089	0.8770	133.6	0.8576
SI15K	1.4783	591.15	2.3948	0.8929	86.80	0.0554
SI15M	1.4820	591.15	2.4319	0.8580	43.65	0.0440
SI15L	1.4796	591.15	2.2564	0.8772	67.30	0.0472
SI15N	1.4691	592.15	2.2650	0.9070	50.94	0.0379
SI15O	1.4742	594.15	3.1418	0.8688	33.68	0.0455
SI15Q	1.4617	591.15	2.4200	0.9011	16.48	0.0247
SI15P	1.4596	591.15	2.7280	0.9276	25.39	0.0312
Avgs	1.4729	591.5	2.3871	0.9015		

Table 5.1 continued.

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
SI20A	1.4648	592.15	2.6142	1.2235	31.95	0.0367
SI20C	1.4523	591.15	2.6342	1.2535	15.84	0.0227
SI20B	1.4596	591.15	2.8231	1.2738	24.47	0.0327
Avgs	1.45909	591.5	2.6905	1.2503		
SI25A	1.4832	591.15	2.3777	1.4018	31.35	0.0336
SI25B	1.3477	591.15	2.3123	1.6016	23.64	0.0166
SI25C	1.4756	593.15	2.6590	1.3233	15.93	0.0232
Avgs	1.4795	592.2	2.5184	1.3626		
SI30A	1.4832	591.15	2.5436	1.7430	30.60	0.0306
SI30B	1.4814	592.15	2.1694	1.7752	23.73	0.0295
SI30C	1.4826	593.15	1.9308	1.7534	15.45	0.0223
Avgs	1.4824	592.2	2.2146	1.7572		
SI35A	1.4767	593.15	2.4213	2.0464	15.18	0.0218
SI35B	1.4791	593.15	2.5302	2.0267	23.50	0.0267
SI35C	1.4767	593.15	2.7816	1.9433	30.52	0.0280
Avgs	1.4776	593.2	2.5777	2.0055		

Table 5.2 **Sulphur Initial Rate Data**

Pressure = 1.49352 * 10^5 Pa

Temperature = 592 K

Water = 3489 Pa

Model: Y = A tanh (B X)

Data Set	A	B	A*B mol/g hr * 100	ppS_2 Pa	sum of sqs
SI04	0.1385	0.5300	7.3405	266.9	$1.388*10^{-4}$
SI05	0.1370	0.6201	8.4954	364.6	$4.806*10^{-5}$
SI06	0.1247	0.8152	10.165	447.3	$2.379*10^{-5}$
SI08	0.0911	0.9947	9.059	600.0	$2.329*10^{-4}$
SI10	0.07081	1.658	11.740	893.7	$1.603*10^{-4}$
SI15	0.05499	2.567	14.116	1345	$2.129*10^{-4}$
SI20	0.04586	3.516	16.124	1848	$9.622*10^{-7}$
SI25	0.03802	4.459	16.953	2043	$3.802*10^{-11}$
SI30	0.03353	5.365	18.989	2639	$1.147*10^{-6}$
SI35	0.02937	6.353	18.659	3077	$8.954*10^{-7}$

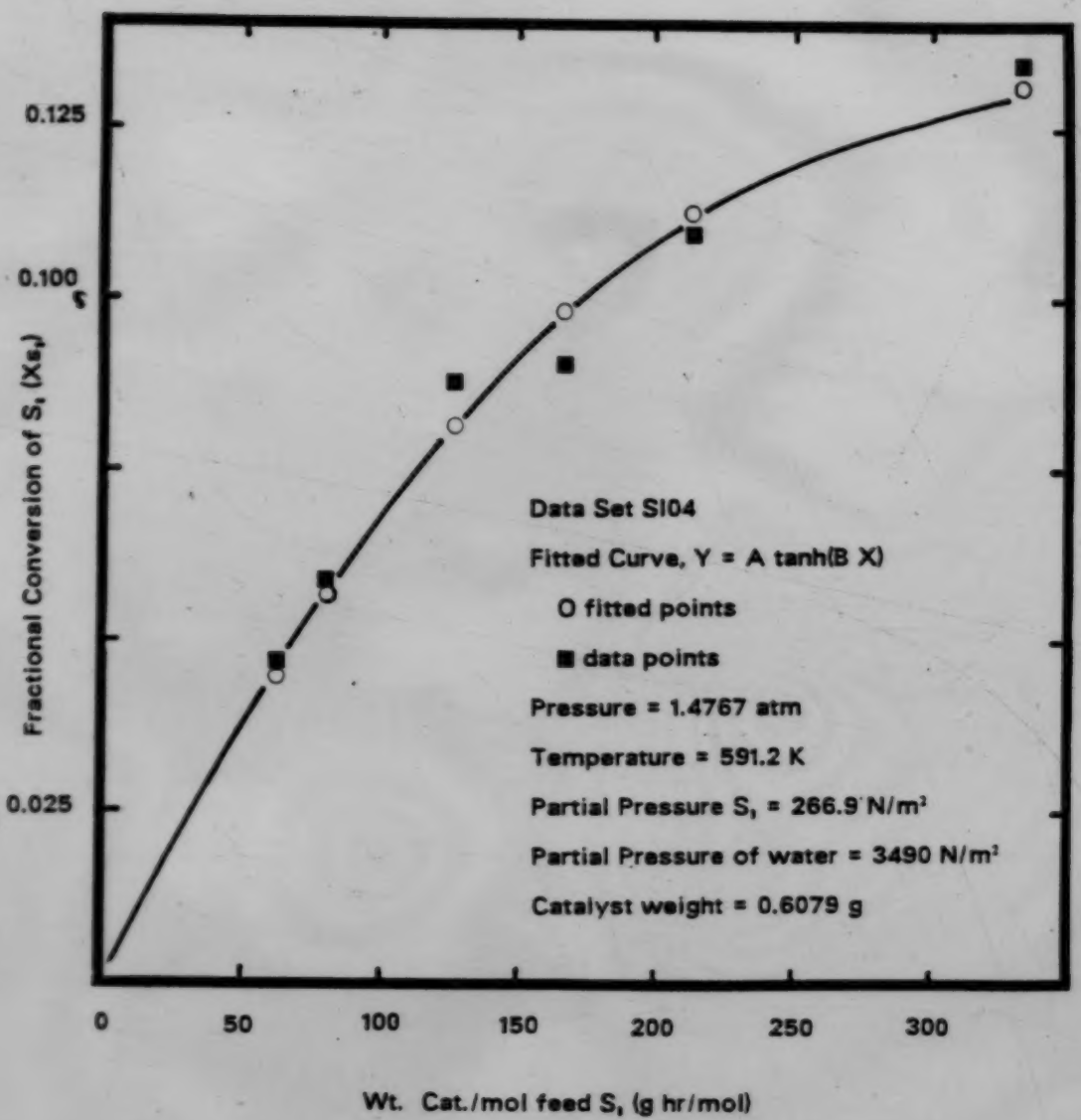


Figure 5.1 Sulphur Initial Rate Plot

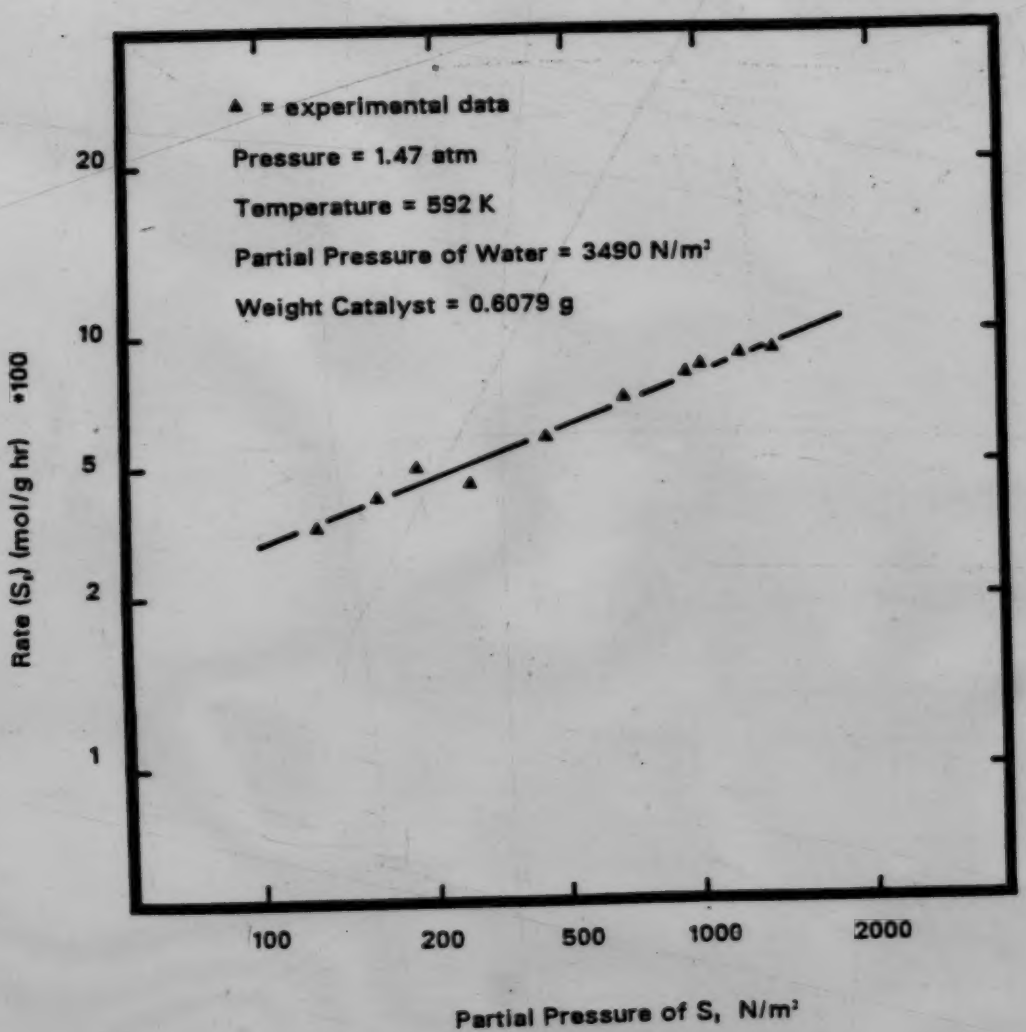


Figure 5.2 Order with Respect to Sulphur

5.3 Analysis of WI data

A total of 51 finite rate data points were obtained in order to derive the initial rates used to establish the water dependence of the reaction. Some 8 of these were discarded and were not used in the determination of the initial rates. The conversions of runs WI06C, WI08C, WI10C, WI12C, WI15C and WI15D were all suspected as being too low and when they were repeated, this suspicion was confirmed. These runs were all performed consecutively and the probable cause of the error was problems with the sulphur feeder. It is likely that the "low" range of sulphur syringe gears had been erroneously engaged. This would result in less reaction than would be expected at the assumed sulphur feed rate and as a result the conversions were correspondingly low.

The conversion calculated for the run WI06F is 20% less than would be predicted by a smooth curve through the remaining data. An analysis of the raw data indicates that the molar feed rate of water was more than 10% less than the average for the run. This compares with a variation of ±5% for the other water feeds. As a consequence, this datum was not included in the initial rate analysis.

The WI data sets are analysed in the same way as the SI data. Due to the more flexible control of the water flow rate, it was possible to obtain at least five and usually six separate data for each data set. Unfortunately however, the proximity to the origin was limited by the sulphur flow rates which were fixed.

A summary of the space time/conversion data is given in Table 5.3 below. Figure 5.3 illustrates the experimental data for the data set WI01. The initial rates that are derived from the experimental data are given in Table 5.4. The full fitted data are given in the Appendix.

Figure 5.4 illustrates the logarithmic relationship between rate and water partial pressure. The data have been fitted by eye and a curvilinear relationship has been assumed.

TABLE 5.3 DATA SETS WI (summary)

RUN	PRESSURE Atm	TEMP K	WATER percent	SULPHUR percent	Wt/MOLES g hr/mol	X Conversion
WI01A	1.4737	593.15	1.1436	0.4846	47.52	0.1357
WI01B	1.4710	592.15	0.9815	0.4898	35.17	0.1113
WI01C	1.4648	591.15	0.9918	0.5040	27.69	0.1114
WI01D	1.4753	593.15	1.0381	0.5048	17.46	0.0957
WI01E	1.4761	591.15	1.0070	0.5055	13.77	0.0843
WI01F	1.4708	591.15	0.9819	0.5131	36.39	0.1208
Avgs	1.4720	592.2	1.0266	0.5006		
WI02A	1.4714	593.15	2.2368	0.4906	24.55	0.1242
WI02B	1.4612	593.15	1.8135	0.4998	19.46	0.1044
WI02C	1.4730	592.15	1.9366	0.5031	14.25	0.0961
WI02D	1.4722	591.15	1.8204	0.5051	9.84	0.0756
WI02E	1.4761	593.15	2.0106	0.4986	6.89	0.0587
WI02F	1.4720	591.15	1.8234	0.5141	19.63	0.0987
WI02G	1.4696	591.15	1.9071	0.3945	14.92	0.0995
Avgs	1.4708	592.2	1.9355	0.4865		
WI04A	1.4737	593.15	3.9481	0.4905	13.91	0.1103
WI04B	1.4652	592.15	3.3993	0.4953	10.24	0.0964
WI04C	1.4730	591.15	3.7166	0.5073	7.438	0.0838
WI04D	1.4722	593.15	3.3023	0.5024	5.46	0.0636
WI04E	1.4761	593.15	3.6638	0.5063	3.83	0.0501
Avgs	1.4721	592.4	3.6820	0.4999		

Table 5.3 continued.

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
WI06A	1.4648	591.15	5.7800	0.4968	9.48	0.11416
WI06B	1.4531	591.15	5.4334	0.5137	6.57	0.09410
WI06C	1.4742	591.15	5.3927	0.5039	5.09	0.04214
WI06D	1.4664	593.15	5.2939	0.5103	3.45	0.05877
WI06E	1.4702	593.15	5.6162	0.5096	2.51	0.04911
WI06F	1.4696	591.15	4.9378	0.5189	5.70	0.06596
Avgs	1.4637	592.2	5.5310	0.5076		
WI08A	1.4652	591.15	7.0672	0.4981	7.77	0.09028
WI08B	1.4519	591.15	6.8031	0.5188	5.29	0.07833
WI08C	1.4730	591.15	7.8088	0.5039	3.51	0.04519
WI08D	1.4687	593.15	7.7498	0.5671	2.58	0.05138
WI08E	1.4772	593.15	7.5824	0.5082	1.86	0.04358
WI08F	1.4696	591.15	7.5663	0.5163	3.70	0.06404
Avgs	1.4666	592.0	7.4338	0.5187		
WI10A	1.4628	592.15	8.7717	0.5011	6.330	0.11130
WI10B	1.4531	591.15	9.0704	0.5196	3.976	0.07023
WI10C	1.4648	593.15	9.4982	0.5041	2.920	0.03694
WI10D	1.4746	592.15	9.6183	0.5161	1.910	0.04455
WI10E	1.4761	593.15	9.6578	0.5100	1.465	0.03187
WI10F	1.4720	591.15	9.2684	0.5183	3.889	0.06786
WI10G	1.4708	591.15	9.3607	0.5170	3.002	0.05797
Avgs	1.4695	591.8	9.3951	0.5162		

Table 5.3 continued,

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
WI12A	1.4616	593.15	11.6000	0.4872	4.702	0.09142
WI12B	1.4554	592.15	11.4576	0.5135	3.134	0.06651
WI12C	1.4730	592.15	11.4909	0.4967	2.371	0.03074
WI12D	1.4746	592.15	11.7187	0.5112	1.555	0.03831
WI12E	1.4749	593.15	11.3656	0.5134	1.250	0.03285
WI12F	1.4708	591.15	12.3749	0.5096	2.879	0.06362
WI12G	1.4696	591.15	12.1966	0.5152	2.296	0.05043
Avgs	1.4692	592.0	11.823	0.5126		
WI15A	1.4616	593.15	14.2480	0.4875	3.83	0.07816
WI15B	1.4554	591.15	14.3046	0.5180	2.51	0.06148
WI15C	1.4730	593.15	14.0629	0.4950	1.94	0.02909
WI15D	1.4722	593.15	14.1088	0.4975	1.26	0.01844
WI15E	1.4725	593.15	14.9369	0.5131	0.95	0.02700
WI15G	1.4696	591.15	1.37828	0.4930	1.95	0.04322
avgs	1.4677	592.2	14.318	0.5029		

Table 5.4 **Water Initial Rate Data**

Pressure = 1.48810 * 10^5 Pa

Temperature = 592 K

Sulphur = 756 Pa

Model: Y= A tanh (B X)

Data Set	A	B	A*B mol/g hr * 1000	PP water Pa	sum of sqs
WI01	0.1262	0.05544	6.9965	1536.5	$2.397*10^{-4}$
WI02	0.1218	0.07327	8.9243	2880.2	$2.098*10^{-4}$
WI04	0.1197	0.1127	13.4902	5479.1	$1.223*10^{-3}$
WI06	0.1272	0.1496	19.0291	8230.7	$1.837*10^{-3}$
WI08	0.09271	0.2442	22.6400	11062	$2.883*10^{-3}$
WI10	0.1883	0.1046	19.6962	13981	$1.186*10^{-4}$
WI12	0.1198	0.2051	24.5711	17594	$1.657*10^{-3}$
WI15	0.1069	0.2447	261582	21307	$3.402*10^{-3}$

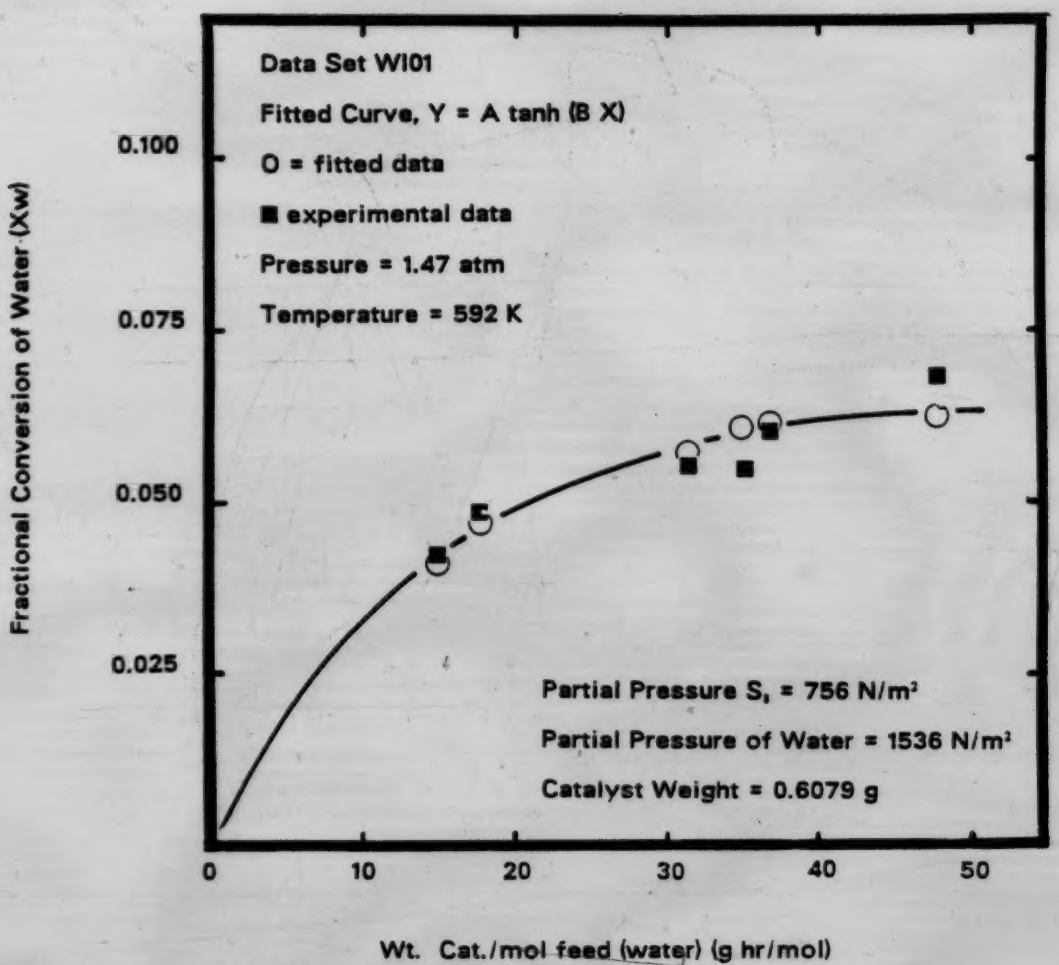


Figure 5.3 Water Initial Rate Plot

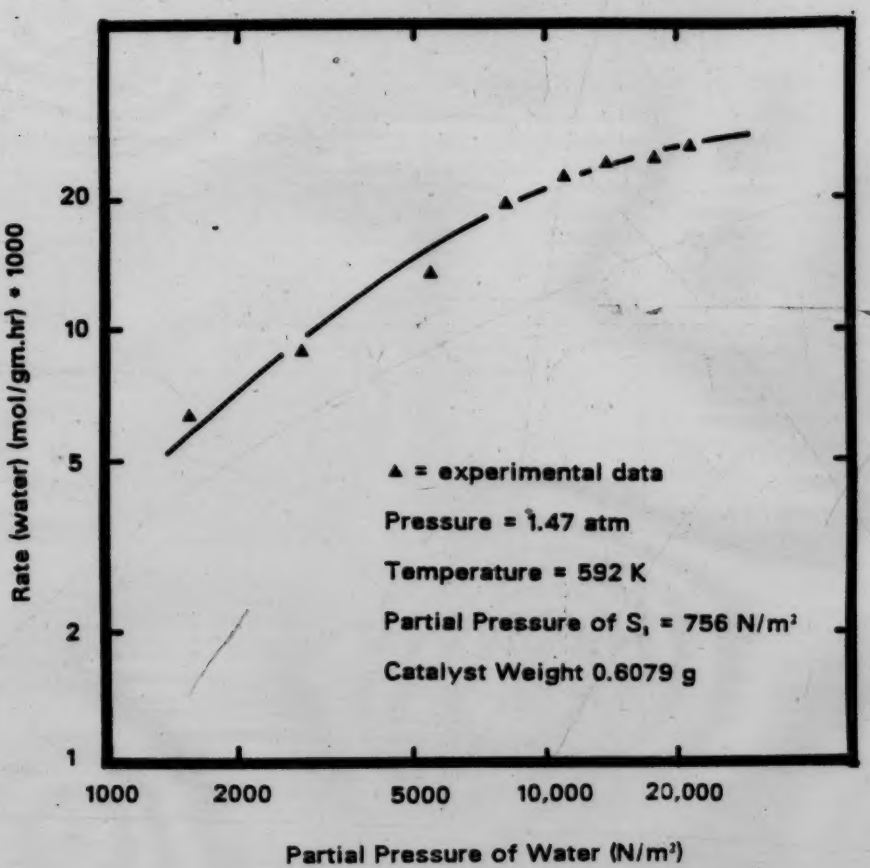


Figure 5.4 Logarithmic Plot of Rate versus Water Partial Pressure

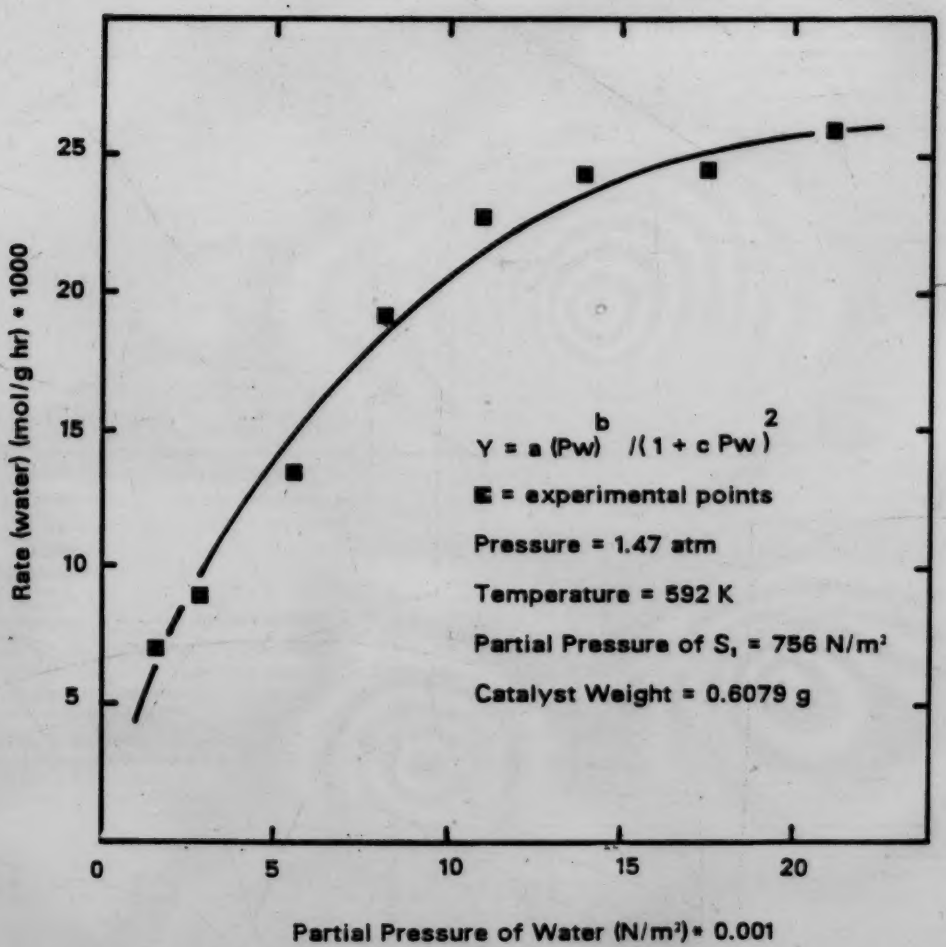


Figure 5.5 Rate (water) versus Water Partial Pressure)

Figure 5.5 illustrates the relationship between the partial pressure of water and the reaction rate. This curve is the fit given by the modified damped least squares method (Meyer and Roth (58), see Appendix 3) of the function ;

$$f(\ ) = a\,(Pw)^{b} * [1 + c\,(Pw)]^{-n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

where n = 0,½,1,2,3

In order for the computer program to run successfully, it was necessary to scale the initial rate data so that the dependent and independent variables were of the same order of magnitude. This was done by multiplying the rate of reaction by 10 and dividing the partial pressure by 10000. The actual function being fitted is therefore ;

$$f(\ ) = -Rw * 10 = a\,(Pw/10^{4})^{b} / [1 + c\,(Pw/10^{4})]^{n} \qquad \ldots\ldots\ldots \quad (5.2)$$

Table 5.5 shows the values of the parameters that were obtained after descaling the results of the program.

Table 5.5 Comparison of Rate Equation Parameters

n	a	$k_2 * 10^7$	b	$c(K_2 * 10^4)$	Sum of Sqs.
0	0.1925	117.84	0.5228	0.0000	$2.327 * 10^{-3}$
½	0.2839	28.367	0.7196	1040	$1.032 * 10^{-3}$
1	0.3557	7.3238	0.8790	0.7461	$6.907 * 10^{-4}$
2	0.3358	6.9140	0.8911	0.2742	$5.449 * 10^{-4}$
3	0.3215	6.1696	0.8751	0.1576	$5.170 * 10^{-4}$

The choice of scaling factors affects the solution obtained. However, a thorough investigation of the effect of different sets of scaling factors determined that those chosen gave the lowest sum of squares. An alternative solution reached by scaling the partial pressure by a factor of 100 and the rate by 1000, results in an order for water of about 2. The log-log plot of this data (Figure 5.4) does not give a straight line, indicating the retarding influence of the denominator term on the rate. The slope of this

line as Pw --> 0 will be the order of the reaction with respect to water. Taking the first three points of the plot, the slope is about 0.7, and this permits both orders of 1 and 2 to be valid. The value of 1 is the more probable.

The parameters estimated by the program are the "a", "b" and "c" in equation 5.3 above. The parameter "a" is equal to the rate constant times the sulphur partial pressure, ($k_1 Ps^x$, where "x" has been determined to be 0.39, from the SI data analysis). Thus the "k_1" in Table 5.5 is the rate constant of the reaction as calculated from the partial pressure of sulphur. Parameter "b" is the order of the reaction with respect to water. Parameter "c" corresponds to the water adsorption equilibrium constant. It should be borne in mind that this parameter is temperature dependent. No attempt was made to determine the nature of this temperature dependency in this work.

A listing of the main program IRANAL, and the subroutine NLREG is given in Appendix 3.

5.4 Analysis of Temperature Data

Two additional data sets were obtained at higher temperatures. A summary of the experimental data is shown in Table 5.8. Note that the data set WT6L is the same as the set WI06. Table 5.7 lists the initial rate data. The data was analysed in light of both of the previous data and the rate constant derived from that data.

The rate constants were calculated from the initial rate data by substituting the values of the kinetic parameters obtained in the rate equation, viz.

$$k_2 = -Rw\,[1 + 0.2742\,(Pw)]^3 / [(Ps)^{0.39}\,(Pw)^{0.99}] \quad \ldots\ldots\ldots \quad (5.3)$$

The constant in the rate equation denominator is also temperature dependent but is assumed to be constant. Table 5.8 shows this data. Figure 5.6 shows the plot of log k_1 against reciprocal temperature. This figure indicates the straight line relationship that exists between these quantities.

Table 5.6 Space Time Data at 654 K, 623 K and 592 K

RUN	PRESSURE	TEMP	WATER	SULPHUR	Wt/MOLES	X
	Atm	K	percent	percent	g hr/mol	Conversion
WT6HA	1.4676	653.15	6.0065	0.2882	8.79	0.23271
WT6HB	1.4712	653.15	5.7703	0.2948	5.90	0.18592
WT6HC	1.4700	653.15	5.8999	0.2972	4.53	0.19119
WT6HD	1.4629	653.15	5.9485	0.3007	2.95	0.14256
WT6HE	1.4712	653.15	5.8035	0.2971	2.32	0.12032
Avgs	1.4687	653.2	5.8857	0.2956		
WT6MA	1.4709	624.15	6.2727	0.3668	8.31	0.19677
WT6MB	1.4709	624.15	6.1704	0.3788	5.49	0.15534
WT6MC	1.4650	624.15	5.8092	0.3800	4.57	0.13203
WT6MD	1.4639	624.15	5.3953	0.4016	3.35	0.10042
WT6ME	1.4639	624.15	5.8065	0.3780	2.29	0.07618
Avgs	1.4670	624.3	5.8908	0.3810		
WT6LA	1.4648	591.15	5.7800	0.4968	9.48	0.11416
WT6LB	1.4531	591.15	5.4334	0.5137	6.57	0.09410
WT6LC	1.4742	591.15	5.3927	0.5039	5.09	0.04214
WT6LD	1.4664	593.15	5.2939	0.5103	3.45	0.05877
WT6LE	1.4702	593.15	5.6162	0.5096	2.51	0.04911
WT6LF	1.4708	591.15	5.6752	0.5136	6.30	0.06264
WT6LG	1.4696	591.15	4.9378	0.5189	5.70	0.06596
avgs	1.4637	592.2	5.5319	0.5080		

Table 5.7 **Temperature Initial Rate Data**

Pressure = $1.4670 * 10^5$ Pa

Temperature = 592 K, 624 K and 653 K

Data Set	A	B	A * B mol/g hr *100	PP S, Pa	PP water Pa	sum of sqs
WT6L	0.1271	0.1498	1.9040	753	8204	$1.917*10^{-4}$
WT6M	0.2441	0.1346	3.2856	566	8756	$2.454*10^{-4}$
WT6H	0.2296	0.2437	5.5954	440	8759	$5.185*10^{-4}$

Table 5.8 **Activation Energy Data**

T (K)	Rate W mol/g hr	Water pp Pa	Sulphur pp Pa	k 10^7 $(K)^{-1}$	ln(k)	1/T
592.2	0.019040	8204	753	7.0154	-14.170	$1.6886 * 10^{-3}$
624.2	0.03286	8756	566	13.088	-13.546	$1.60205 * 10^{-3}$
653.2	0.056562	8759	440	24.848	-12.905	$1.53093 * 10^{-3}$

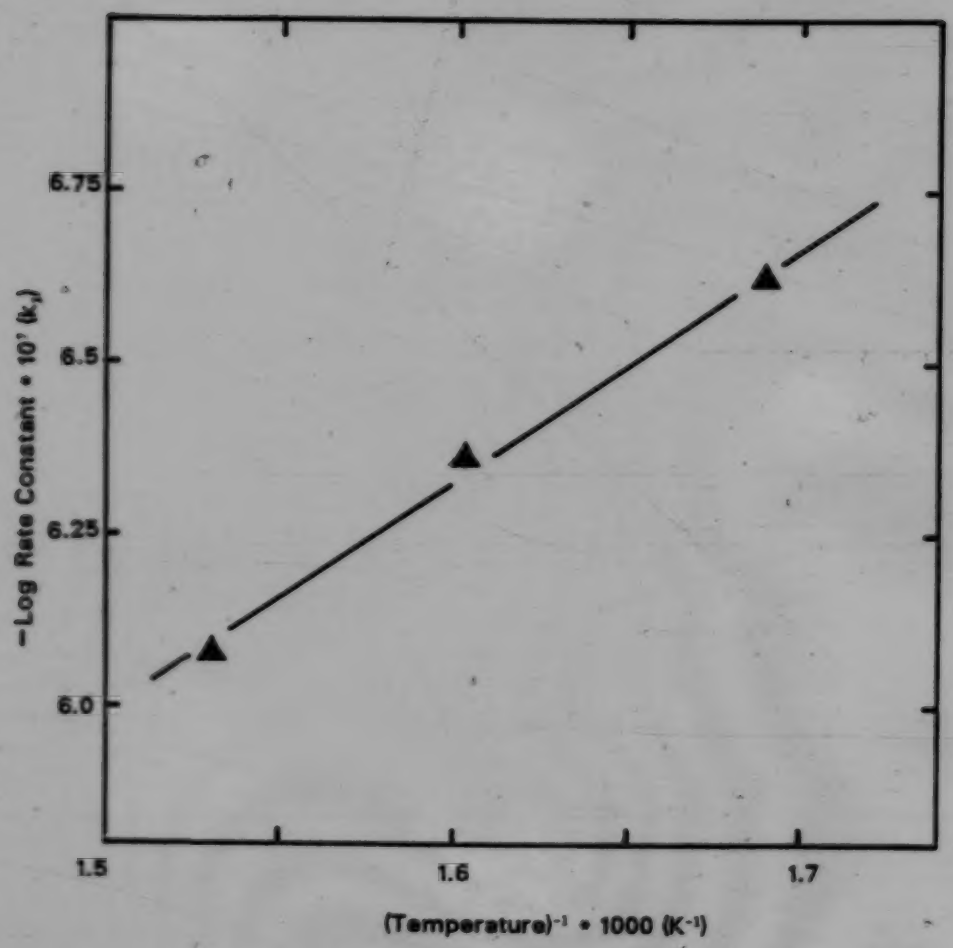


Figure 5.6 Temperature Dependence

Taking the natural logarithm and calculating the slope of this line gives the quantity −E/R, the ratio of the activation energy to the gas constant. The intercept of this line is equal to the natural log of the Arrhenius parameter A.

Thus,

$$-E/R = -7994\ K$$

$$A = 0.5004 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5.4)$$

5.5 Thermodynamic Equilibria

The first 51 experimental runs were performed at low space velocities and high catalyst loadings. Under such conditions, the reaction goes virtually to completion and the equilibrium state is approached. These runs were basically of a preliminary nature, being used to investigate the operating characteristics of the experimental system. They are therefore subject to greater error than the later experimental runs, and there is considerable scatter. In particular, the measurements of temperature and compositions contain more uncertainty and these will affect the calculated equilibrium to a greater extent than, for example, the uncertainty in the actual flow rate, since the flow rate has little effect on the conversion in this regime.

Figure 5.7 illustrates the data used to estimate the experimental equilibria. The experimental equilibria are estimated by a "free−hand" fit of the data, since the data displays a high degree of scatter. However, the trend of the data is quite clear. The conversion of water has been plotted in comparison with the thermodynamically calculated equilibria at the same temperature pressure and feed composition. Table 5.9 illustrates the various equilibria that were estimated from Figure 5.7 (Exptl Xw) and those obtained from the thermodynamic calculations (Equil Xw).

Table 5.9 **Comparison of Equilibria**

Sulphur(8)%	Expti Xw	Equil Xw
0.1654	0.180	0.128
0.2239	0.190	0.132
0.2758	0.205	0.138
0.4000	0.210	0.147
0.6218	0.250	0.156
0.8912	0.280	0.161

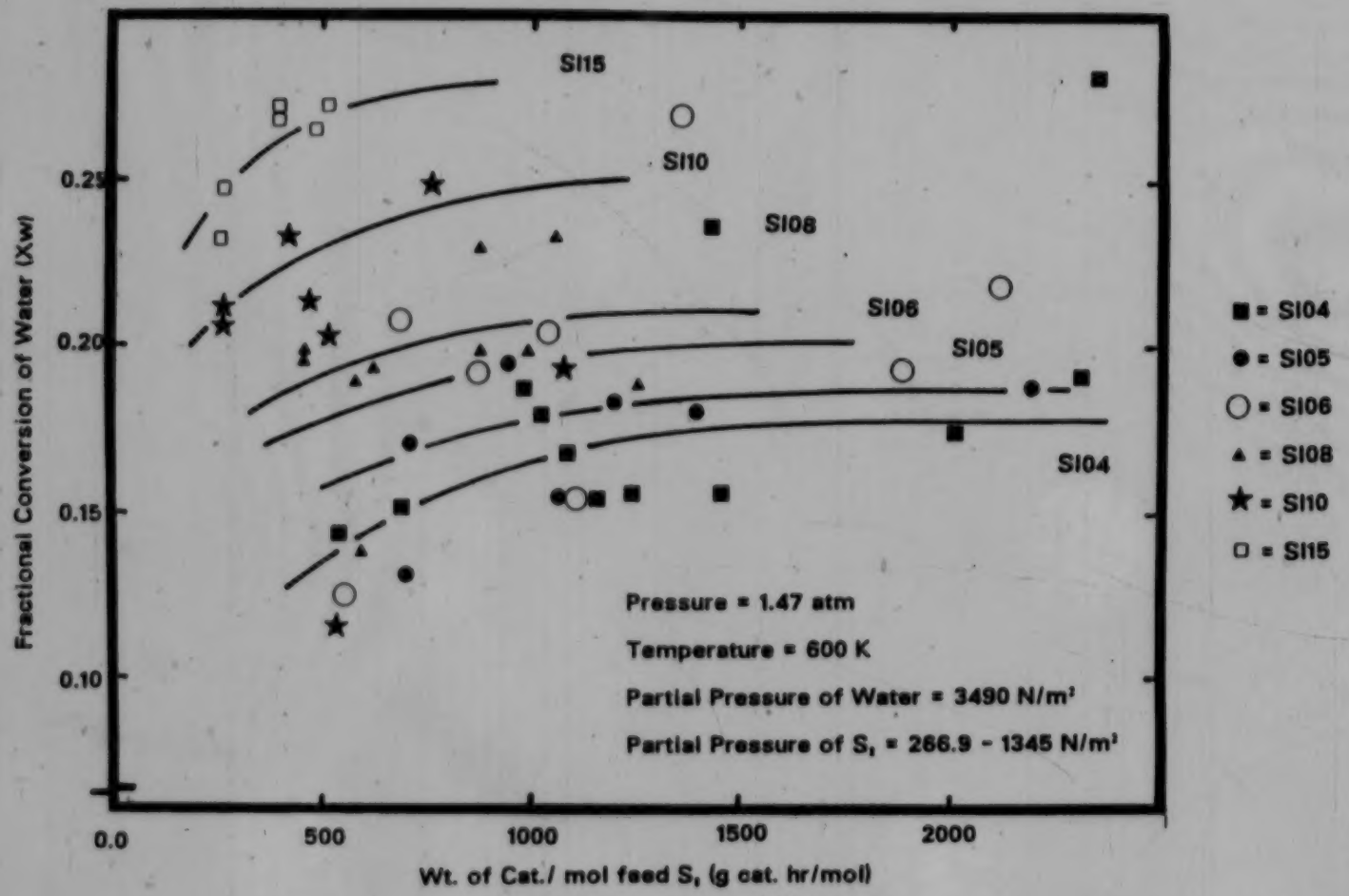


Figure 5.7 Experimental Equilibria

5.6 Discussion

5.6.1 Discussion of Errors

The study of the kinetics of a reversible reaction can be made from either side of the equilibrium. When the equilibrium of the reaction lies well to one side at the temperature of interest, the kinetic study is complicated by the necessity of obtaining precise data on the minority products which may be present only in small very amounts. In the case of the Claus reaction, the equilibrium conversion of H_2S is around 90% at 600 K so that the maximum mole fraction of H_2S is only about 0.1. In an initial rate study, the data must be obtained as far from equilibrium as possible and so in the case of this reaction, the reaction products H_2S and SO_2, are less than 1 % of the reactor product stream. As a result, the major uncertainties associated with the collection of the experimental data are contained in the product analysis. The average percentage uncertainty in the measurement of the G.C. peak areas are for H_2S, SO_2 and H_2O respectively, 2.46, 3.38 and 2.65 %. The uncertainties in the other experimental measurements are small, being less than 1 %, except in the case of the Differential Pressure recorder which included an uncertainty in reading the instrument of about 4 % at low scale deflections, viz,

Scale reading 5 ± 0.2 ⟶ 4 % error

Since the volumetric flow rate is proportional to the square root of the scale deflection, the actual error is 2 %.

Similarly :

Pf, Scale reading 9.0 ± 0.1 ⟶ 1.1 % error

Patm, " " 700 mmHg ± 0.1 ⟶ 0.014 % error

Pr, " " 46.0 ± 0.2 ⟶ 0.4 % error

Tf, " " 6.0 ± 0.2 ⟶ 1 K error

Tr, " " 45.0 ± 0.2 ⟶ 2 K error

The average uncertainty in the sulphur and water feeds are 1.8 and 1.7 % respectively.

The most significant uncertainty in the data was caused by the operation of the water and sulphur feeders. The operation of the water feeder alone produced a steady flow, as evidenced by the fact that the repeatability of the G.C. peak area test (Section 4.2.5), which determined that the fluctuations due to the water feeder were 2.87%, was similar to the accuracy determined by the G.C. calibration, (2.65%). The sulphur feeder calibration data (Appendix 1), show that the sulphur flow uncertainty was not affected by the choice of flow rate. As a result, it is not possible to explain the unevenness in the water product by considering the water and sulphur feeders individually. The source of the uncertainty in the product analysis must derive from either the use of the two feeders at once, or the effect that the vapourisation of sulphur had on the flow. Since it was not known whether the sulphur feed actually affected the water feed or not, the water feed was determined in the analysis by back calculating from the products, using stoichiometry and the G.C. calibrations. This calculation will not eliminate the error involved in the analysis since only the H_2S component was used to calculate the H_2O in the feed , and the overall mass balance could still be checked using the SO_2 component.

There are two methods that may be used to estimate the uncertainty associated with the data ;

1. Calculation of the H_2S/SO_2 mole ratio.
2. Calculation of the oxygen g-atom balance over each run.

The H_2S/SO_2 mole ratio throughout the course of this study was within 5% of 2, the stoichiometric ratio. This ratio determines that the Claus reaction stoichiometry is being followed. The calculation of the product sulphur and the feed water using this stoichiometry is therefore valid.

The difference in the g-atom balance on oxygen is around 3%. This indicates that the mass balance across the reactor is correct since there was no source of oxygen except in the feed water and the oxygen balance has been calculated from the product mole flow rates assuming Claus reaction stoichiometry. The g-atom balance on hydrogen produces slightly larger differences than the oxygen balance, about 3.5%. This figure illustrates the error associated with calculating the mole flow rates from the H_2S and SO_2 G.C. peaks

As would be expected, because the water feed rate is increasing in the WI data sets, the percentage uncertainty decreases with increasing water feed, since the relative size of the H_2S component to the water is much less.

Alternative sources of error include questioning the validity of using the Gibbs free energy minimisation technique to estimate the equilibrium distribution of the sulphur species, especially as these results have been proven to be inexact. There is as yet no other method of directly measuring the sulphur species distribution and as a consequence, no method of measuring the uncertainty of this method. It is assumed to be small in comparison with the errors associated with the product analysis.

It is evident that there is only a small amount of error associated with the mass balance across the reactor. However, an additional source of error is introduced by the uncertainty in the feed flow rates of water and sulphur. The average variation in the water feed rate for the SI data sets was 9.4%. The variation in the sulphur flow rates was 3.6%. The corresponding figures for the WI data sets were 4.0 and 2.9% respectively. The much smaller error in the water feed rates for the WI data sets is due to the much higher water feed rates employed. The average uncertainty in the SI data is therefore about 10% and in the WI data set, 5%. How these uncertainties affect the initial rates is not simply determined since each individual datum has a variable influence on the slope and shape of the fitted curve according to its position. To estimate the uncertainty in the initial rate data it is simpler to look at the data itself.

The variance of the slope of the line is given by, (40),

$$Sb^2 = (Sylx)^2 / \quad (x - x)^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.5)$$

and the confidence band for the slope is given by,

$$b \pm t\, Sb,$$

where t is obtained from the "t" distribution. In the case of the log-log plot of the SI data, Figure 5.2, with 10 data points, there are 8 degrees of freedom. At the 90% confidence level, the slope of the line is,

$$0.397 \pm 0.047 \ (12\%)$$

The errors associated with the WI data sets are less than those with the SI data sets. The average fit variance of Figure 5.5 is 2.6%, the maximum variance being in the point closest the origin. Such a low variance is a result of the fact that 3 parameters were used to fit the data. This is evidenced by the fact that only a small improvement in the value of the sum of squares is achieved with increasing power of the denominator term. The uncertainty in the finite rate data is 7%, so that the uncertainty in the derived kinetic parameters must be at least 7%. As a consequence, the values of the parameters will be rounded off to two significant figures.

The WT data are subject to the same magnitude of error as the WI06 data set. The rate constants are therefore subject to a compounded error of 15% (85). The activation energy is calculated from only three points, the linear alignment of which is plainly fortuitous, as can be seen from the foregoing analysis. The error in the activation energy may be calculated using the maximum and minimum values, obtained from the maximum error in the k_1 values of 15 %, thus,

$$-E/R = -7994 \pm 1200 \ K$$

5.6.2 Sulphur Order

The order of the reaction with respect to sulphur was determined to be 0.397. This value was obtained by performing a least squares analysis on all the sulphur initial rate runs. Since the partial pressure of water was 3721 Pa, stoichiometric restrictions,

$$2\ H_2O + 3/8\ S_8 \rightleftharpoons 2\ H_2S + SO_2$$

might be thought to limit the range of the validity of the data for sulphur order derivation to a maximum sulphur (S_8) partial pressure of (3721 * 3/16) Pa, i.e. 698. In taking the logarithms of the rate equation, the following relationship is obtained :

$$\log(-Rs) = \log(k) + a \log(Ps) + \log[f(Pw)]$$

and so the use of all the initial rate data is justified in obtaining the order of the reaction with respect to sulphur, since the water partial pressure term does not affect the slope of the line.

The order with respect to sulphur may be rounded off to 0.4 . The orders of the forward reaction have been found to be equal to one half the stoichiometric coefficient of the species as given by equation 2.7. Although the forward rate equations are essentially empirical , it is reasonable to expect that such a relationship would be found for the reverse reaction orders, since there are thermodynamic restrictions which govern the form of the kinetic equations. These are described by Denbigh (24). The order with respect to sulphur that would be expected following this relationship, is 0.1875. The experimental order is almost twice this. Indeed, it would require an average sulphur species of about 4 to make the order 0.4 by this relationship. Since there is a distribution of sulphur species, it is unreasonable to presume that only S_8 is reacting with water. This shown by the Comparison of Rates section below (5.6.5). If it is assumed that there is decomposition of the sulphur molecules, then the actual Claus reaction may be taking place with sulphur whose average number of atoms is around 4, even although the species S_4 is but a small fraction of the sulphur vapour. There are thermodynamic limitations which will determine the nature of the sulphur species on the surface but as has been said previously, the exact distribution of sulphur species in the vapour is unknown, far less on a solid surface. By this reasoning, the order of the reaction with respect to sulphur would be temperature dependent, increasing with increasing temperature. This effect could be used to determine whether the above argument is valid.

5.6.3 Water Order

Previous work (30,53,56) had established that the rate of the forward Claus reaction was retarded by the effect of water adsorbing on the catalyst surface. It was to be expected, then, that this effect would be observed in this study, and that, as a result, it would not be possible to determine the order of the reaction with respect to water simply by holding the sulphur partial pressure constant and varying the water partial pressure. Therefore, the expected form of equation is fitted to the initial rate equation

and the kinetic parameters are estimated using a least squares analysis.

Table 5.5 contains the results of this technique. The "best fit" of the data is given in the case of n=3, which is marginally more exact than the case of n=2. These two functions are apparently significantly better than the next best fit of n=1. However, the application of the statistical method of discrimination known as the "F" test determined that it was not possible to discriminate between the fits given by n = ½ and higher. The lack of fit of each model is characterised by the sums of squares of the deviations, hence, the ratios of the sums of squares of the residuals to each model to that of n=3 (SSi/SS3) are,

SS0/SS3	SS½/SS3	SS1/SS3	SS2/SS3
4.50	2.00	1.33	1.05

At the 90% confidence level and with 7 degrees of freedom, the test statistic is 2.78. At this confidence level, therefore, it is only possible to state the water is inhibiting the reaction, and that it is not possible to determine the order of the inhibition.

The derivation of these parameters is a matter of some subjective judgment, since numerical techniques cannot guarantee that the global minimum least squares estimate of the parameters will be found. A number of initial guesses were employed and each minimum found, was compared both to the previous minima and the initial guess which achieved the lowest minimum was noted.

It was necessary to scale the data in order for the method to converge. It would converge rapidly and reliably for these functions when the maximum value was below 10. For this reason, the rates were multiplied by 10 and the partial pressure divided by 10000. The allowance that must be made for the scaling values is illustrated in Appendix 2 in the Calculation of rate constants section.

Uncertainty in the data for the water runs is less than that contained in the sulphur run data. This was probably due to the low flow rate of sulphur employed and this would lessen errors due to sulphur vapourisation and equilibration uncertainties. In addition, the higher water flows employed allowed a larger margin of absolute error. The greater

accuracy permits the simultaneous evaluation of three kinetic parameters with some degree of confidence.

Allowing for the 7 % error that attends the fit of the model to the water initial rate data and noting that the tendency of the model will be to reduce the order of the reaction with respect to water, the order of the reaction with respect to water may be rounded off to 1. This agrees with the one half times the stoichiometric coefficient relationship that is suggested by studies on the forward reaction. This lends a measure of credibility to the suggestion that the sulphur order may be related to a lower order sulphur molecule than S_8. The log–log plot, Figure 5.4, although showing a curve indicates that the order with respect to water is greater than 0.7, since this is the limiting slope of the experimental data. This supports the non–linear regression result that the order is 1. This is evidence that the parameters derived by the method are not spurious.

The denominator parameter K_2, has the value $2.472 * 10^{-5}$ where the units are $(Pa)^{-1}$. The corresponding values from Liu and McGregor's work on the forward reaction are 0.00600 and 0.00433 respectively, units $(mm\ Hg)^{-1}$. In comparable units these are eqivalent to $4.5 * 10^{-5}$ and $3.18 * 10^{-5}$. The adsorption terms are of a similar order of magnitude .The term is temperature dependent since it corresponds to an adsorption term, and so it is expected that with increasing temperature it will decrease. This work was performed at 592 K whereas the previous work was carried out at about 530 K, so this trend is reflected. This is in spite of the fact that three different catalysts, Porocel, a commercial bauxite, and 2 gamma–aluminas, Alon and Kaiser S–201 (this work), are employed.

5.6.4 Temperature Variation

Figure 5.6 illustrates the variation of the rate constant with temperature. The activation energy derived from this is 66.5 kJ . Only three temperatures were available and so only three data points are used to derive the activation energy: this value, therefore, has a limited range of validity. The lower temperature was limited by the dew point of the sulphur vapour because it was desirable to operate significantly above this in order to ensure that condensation of sulphur would not occur. The maximum temperature was limited by the high temperature cut–out protection of the reactor. This

could have been adjusted but would have required a significant rebuilding of the controller – an undesirable step at the late stage in the study.

Calculation of the rate constant at the lowest temperature can be done in two ways: either directly from the measured rate of reaction, or else from the "a" parameter derived from the water data reduction.

$$k(rate) = 6.4606 * 10^{-7}$$

$$k(a) = 7.0154 * 10^{-7}$$

The difference, which is 8 %, measures the difference between the rate function, which includes the reaction order with respect to sulphur, and the experimental function. This is a measure of the consistency .

The degree of uncertainty that should be ascribed to the activation energy is a function of the accuracy with which the rate constant is measured. This is estimated to be about 15 %, which leads to approximately 26 % error in the activation energy.

The activation energy may be compared to the activation energies for the forward reaction. These have a value of 30.1 kJ in the case of McGregor's studies and 30.75 for Liu's work. Since the Claus reaction is exothermic there ought to be a higher activation energy for the reverse reaction. Allowing for the degree of error that is associated with the activation energy derived in this study, these are of comparable magnitude. The reverse reaction activation energy ought to differ from the forward activation energy by the heat of reaction which is in this case is about 100 kJ/mol, so there is plainly a large discrepancy involved, which is not explained by the fact that a different catalyst is being employed. The error associated with the activation energy calculation is large however, the maximum value of the activation energy is only 80 kJ which is 50 kJ less than the value that is implied from the forward reaction activation energies and the heat of reaction. Obviously, it would be advantageous to repeat the initial rate runs using more temperatures in an effort to re-assess this data.

5.6.5 Comparison of Rates

It would be expected that the calculated rates with respect to either component ought to be in stoichiometric ratio to the other since only the Claus reaction is taking place. However, this is not the case since the rate with respect to sulphur (8) neglects the components of the overall sulphur reaction rate that is due to the other sulphur species. The rates of all the sulphur species were calculated and the overall stoichiometric ratio of water and sulphur rates was calculated. On average, there was a difference of 12.8% in the rates. This difference was found to be correlated with the water feed rate.

A positive deviation shown in Table 5.10 reflects a higher water reaction rate than that expected from simple stoichiometry. The higher the water feed rate, the more the water reaction rate exceeds the stoichiometric rate. This relationship is probably due to uncertainties in the product analysis, particulaly in the water component. It is probably exacerbated by the calculation of the water feed rate from the hydrogen sulphide component, since the error is probably associated with the tailing of the water peak at high mole fractions, and this error would have been minimised if the water feed rate had been measured directly. This deviation represents the limit of accuracy of the experimental data, ie. 13%. Since the error is not random, it will have an effect on the calculation of the kinetic parameters. Since the rate is exaggerated at high mole fractions, the inhibiting effect of water will be reduced. There will also be a tendency to increase the apparent reaction order with respect to water.

Table 5.10 Comparison of Sulphur and Water Rates of Reaction

Data Set	% Deviation	Data Set	% Deviation
SI04	-14.5	WI01	-19.0
SI05	-17.5	WI02	-13.0
SI06	-14.5	WI04	-2.5
SI08	-11.0	WI06	+10.0
SI10	-11.2	WI08	+12.5
SI15	-10.0	WI10	+15.5
SI20	-11.0	WI12	+18.0
SI25	-8.0	WI15	+18.5
SI30	-12.5		
SI35	-11.5		

Appendix 2 contains an example calculation of the rate of the forward reaction. This is compared to the rate of the reverse reaction at identical conditions. The rate of the forward reaction is 9.75 times that of the reverse reaction.

5.6.6 Comparison of Equilibria

As shown by Table 5.9, the thermodynamic equilibria are consistently below the experimentally determined equilibria. This is the same relationship that was noted for the approach to the equilibrium for the forward reaction. It is not possible therefore, to explain the discrepancy between the equilibria in terms of the sulphur species data being too low or too high. These results indicate that a more complicated mechanism may be at work which causes the discrepancy, however, as these data are not very precise and are greatly scattered, they can only be used as an illustration that this relationship may be found.

6. SUMMARY - CONCLUSIONS AND RECOMMENDATIONS

Conclusions – Kinetic results

1. The empirical rate equation for the Claus reaction indicated by this study is :

$$-Rw = A \exp(-E/R\,T)\,(Pw)^{a}\,(Ps_{s})^{b} / [1 + K_2\,Pw]^2$$

where,

$A = 0.5004$

$-E/R = -7994$

$a = 0.89$

$b = 0.39$

$K_2 = 2.742 * 10^{-5}$

Temperature in Kelvin, pressure in Pa, rate in mol/hr g cat..

2. The order of reaction with respect to water is in agreement with the order required by thermodynamics. This is not the case with the sulphur component.
3. Inhibition by water is confirmed by statistical evidence. It was not possible to determine the order of the inhibition.
4. The relative rates of reaction are within 13% of the stoichiometric ratio. There was a correlation between the water feed rate and the error that would depress the inhibition and increase the water order slightly.
5. The parameter K_2, corresponding to an adsorption equilibrium constant, is of the same order of magnitude as those values measured by Liu and McGregor for the case of the forward reaction. This indicates that this work is consistent with the previous work on the forward Claus reaction.
6. The activation energy of the reverse reaction is found to be of comparable order with that for the forward reaction. The activation energy that is calculated indicates that the Reverse Claus reaction is endothermic but the difference in the

forward and reverse activation energies is less than that predicted by the heat of reaction.

7. The experimental equilibria are significantly higher than the thermodynamic equilibria.

Conclusions – Equipment Performance

8. The use of two liquid syringe feeders for the reactant feeds had the advantage that the feed rates could be adjusted rapidly and precisely. However, the combination of the two led to large fluctuations in the water feed, probably due to the sulphur feeder.

9. The Berty reactor operated smoothly and without problems throughout the course of this study, except that a small amount of sulphur back-diffused past the impeller shaft seal and condensed on the water cooled shaft. This was a negligible amount of sulphur and was readily removed.

10. The performance of the sulphur condenser was very sensitive to temperature variation. This problem was successively eliminated by adding secondary condensers. The condensing system as described in this work performed well with only minor plugging occuring in the G.C. line. This was related to a temperature rise in the main condenser.

11. The performance of the gas chromatograph and electronic integrator was in general very good. The Chromosorb 108 column provided excellent separation of the reactor product components. In particular the water response had less "tailing" than had been experienced with other columns such the combination of Poropak S and T used earlier.

12. The G.C. calibration apparatus was awkward to use. In particular, the piston that expelled the gas mixture was extremely difficult to move, even with the aid of a jack. The system allows fairly rapid calibration of the G.C. but is clumsy.

Recommendations

1. The principle source of error in this work is the uncertainty in the feed composition. It is likely that both liquid feeders contributed to this, and in addition, the vapourisation of sulphur may be partly (or wholly) responsible. Further studies should have as a primary objective the establishment of steady feed flows, as evidenced by the product analysis, which ought to be constant, and consistent with a mass balance employing the calibrations. It is therefore suggested that the feasibility of a feed system involving the use of water and sulphur saturators be investigated.
2. The gas chromatograph is a satisfactory method of obtaining the mole fractions of the products on a sulphur free basis. However, with the reverse reaction, sulphur is a significant fraction of the gas mixture and it would be advantageous to be able to measure the sulphur component in order to complete the mass balance. This could be achieved by condensing the sulphur component of a sample product stream over a measured period of time. This would permit the calculation of the mass flow rate of sulphur
3. With regard to the uncertainty in the feed composition, it would be advantageous to measure independently the feed composition rather than relying on the feeder calibrations. This would also enable the smoothness of the feed stream to be monitored. It is therefore recommended that provision be made to measure the mass fraction of sulphur in the feed stream. A similar method to that suggested for the sulphur product measurement might be employed, including G.C. analysis to obtain the water component.
4. It was found in the early stages of this work that much of the tubing and vessels used in building the early versions of the experimental equipment was catalytically active. It is strongly recommended that great care is taken to ensure that only 316 stainless steel is used in the fabrication of equipment for Claus reaction studies and that all tubing and vessels in contact with the reactants be kept scrupulously clean.

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NOMENCLATURE

A	Pre-exponential factor
A	Initial rate parameter
Al^*	Surface Aluminium atom
a	order with respect to water
$a\psi$	exterior surface area * shape factor, m^2 / m^3(bed)
b	order with respect to sulphur
B	initial rate parameter
c	rate equation parameter
Cp	specific heat, J/Kg K
Dp	catalyst particle diameter, m
Dim	diffusion coefficient, m^3/s
E	activation energy
eq	equilibrium
Fa	mole flow rate of a, mol/s
f	fugacity
h	heat transfer coefficient W/m^2 K
ΔH	heat of reaction, J/kg mol
k	rate constant
k_1	rate constant of forward reaction
k	mass transfer coefficient, kg mol/m^2 s
k_2	rate constant of reverse reaction
K	equilibrium constant
K_1	equilibrium constant of adsorption term, forward reaction
K_2	equilibrium constant of adsorption term, reverse reaction
L	catalyst bed depth, m

M	molecular weight
$\dot{m}$	mass flow rate, kg/s
$\dot{n}$	absolute reaction rate, kg mol/s
N	mass flux, kg mol/s
P	partial pressure, Pa
Pa	unit of pressure, Pascal (N/m^2)
Patm	atmospheric pressure, mmHg
Pc	critical pressure, atm
Pf	feed pressure
Ph_2s	partial pressure of H_2S, Pa
Pr	Prandtl number
Pr	reactor Pressure
Psn	partial pressure of sulphur, where n is the average size of the sulphur molecule
Pso_2	partial pressure of SO_2, Pa
Ps_x	partial pressure of total sulphur, Pa
Ps_8	partial pressure of S_8, Pa
Pw	partial preassure of H_2O, Pa
Q	heat evolved, J
r	reaction rate, kg mol/s kg cat
-R	rate, g mol/hr g catalyst
$-Rh_2s$	rate with respect to hydrogen sulphide,
-Rs	rate with respect to sulphur (8)
$-Rso_2$	rate with respect to sulphur dioxide
-Rw	rate with respect to water
R	gas constant
Re	Reynolds number
rpm	impeller speed
Sb	standard deviation of the slope
Sylx	standard deviation of y over x
T	temperature, K

Tc	critical temperature, K
Tf	feed temperature, K
Tr	reactor temperature, K
u	chemical potential
Wt	weight of catalyst, g
X	conversion
Xa	conversion of a
x	mean x
γ	fugacity coefficient
μ	viscosity
ρ	density
ϕ	shape factor
ν	stoichiometric coefficient

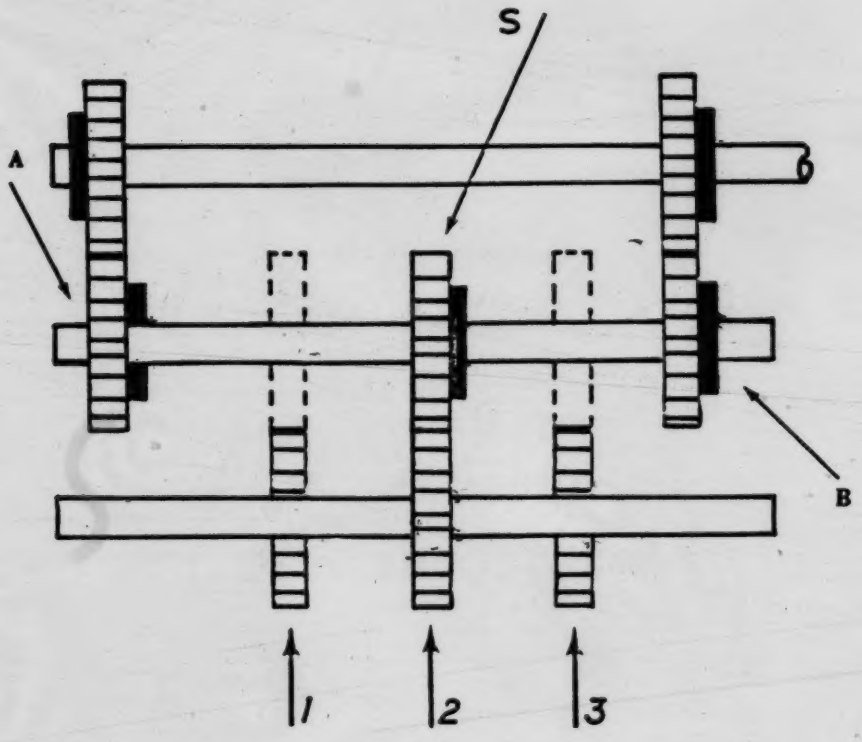
APPENDICES

APPENDIX 1 Calibrations

Calibration of Equipment

1. Sulphur Syringe

Figure A-1.1, Sulphur Feeder Gear Arrangement



Six speeds are possible with the above gear train. These are arranged in the following progression :

Gear A engaged, B disengaged, ⟶ high range

Gear A disengaged,B engaged, ⟶ low range

Gear S engaged with 1, 2 or 3, ⟶ 3 speeds in each range

Calibration was achieved by using the micrometer scale located on the piston rod. Using this scale, it was possible to measure the rate of travel of the syringe piston. This speed could then be correlated to the weight of sulphur expelled from the syringe over the same period of time. The ratio of sulphur weight to distance should be the same for each gear. The Table A-1.1 illustrates the calibration data obtained.

Table A-1.1, Sulphur Feeder Calibration Data

Gear	Mass flow	Piston speed	Ratio	Average flow
	g/hr	cm/min	g/cm	mol S_1 /hr
L1	3.3827	4.486	13.86	1.4937
H1	5.3429	7.376	14.23	2.3952
L2	8.8395	9.6619	14.14	3.0201
H2	10.511	1.4817	14.10	4.6413
L3	13.588	1.9420	14.28	5.9999
H3	21.008	2.9729	14.15	9.2763

The deviation from the mean ratio does not appear to be related to a particular gear or range of gears, and so a "corrected" sulphur flow was calculated using the mean ratio.

The calibration data were obtained at an oven temperature of 135 °C. The length of time for each sampling was not less than 30 minutes. A single comparison run was performed at 173 °C, that is, above the liquid sulphur transition point (75).

H2 1.0507 g/hr 0.14847 cm/min 14.13 g/cm

From this result, it can be seen that the sulphur oven temperature has little effect on the piston operation over this temperature range. It was necessary to ascertain this as the variation of the density of sulphur was not known. In addition, it indicated that the performance of the syringe was independent of the sulphur viscosity, since the viscosity transition temperature is about 159 °C.

2. Water Syringe Feeder

The calibration of this piece of equipment was carried out over the bottom two ranges of the capacity of the instrument, designated 1/1000 and 1/100. These ranges covered the entire range of flows to be used in the kinetic experiments. The advantage of using a large capacity syringe in conjunction with the pump, eg. infrequent refilling, is limited by the ability of the pump motor to generate sufficient power to overcome the added friction. As a result of this limitation, a 20 ml. syringe was used throughout the period of this study. This size was sufficient to accommodate at least one complete run, even at high flow rates.

The calibration was carried out by filling the syringe with distilled water and running the pump over various times of up to six hours in the case of very low flow rates. The discharge was collected in a narrow necked flask. Care was taken to reduce evaporation by using a cotton wool stopper. The loss due to evaporation was estimated by applying Fick's law, assuming saturated vapour above the water surface. The error was estimated to be less than 1%, which was negligible in comparison to the error associated with the pump itself, especially at low flow rates, as shown by Tables A-1.2 and A-1.3.

Eight measurements were made over the entire 1/1000 range, from 100 to 900 percent maximum flow. Six measurements were made over the 1/100 range, from 50 to 500 percent maximum flow. The two sets of data were fitted by a linear least squares regression. The results are shown in the following Tables, A-1.2 and A-1.3

3. Reactor Pressure Transducer

The reactor pressure transducer was calibrated against a mercury manometer open to atmosphere. It was calibrated with the reactor system at the operating temperature in order that variations due to temperature would be minimised. The atmospheric pressure was measured by a barometer. The following Table A-1.5 contains the calibration data obtained.

4. Differential Pressure Cell

The differential pressure cell was calibrated using a precalibrated dry test meter. The system pressure at which the calibration was carried out was set to 8.5 psig, which was approximately the average operating pressure. The calibration data is shown in Table A-1.4

5. Gas Chromatograph

The response of the gas chromatograph to the hydrogen sulphide and the sulphur dioxide components of the product streams was calibrated using sample gas mixtures of known composition. The apparatus used for this is illustrated by Figure A-1.2 and was originally constructed by McGregor(51).

The sample mixing chamber was a five litre capacity lucite cylinder and was equipped with a moveable piston and mixing fan. The lucite cylinder had been calibrated by McGregor and this was checked and found accurate, thus the volume of the cylinder was known as a function of piston position.

Following the calibration procedure as described by Cho (15), the entire calibration apparatus was purged with N_2 for some two hours before use. The cylinder was allowed to fill with pure nitrogen via line A, and was allowed to come to room temperature and pressure. The gas burette and line B were purged with the gas of current interest and a volume of gas was trapped in the gas burette. The height of the mercury reservoir was adjusted to bring the gas in the burette to atmospheric pressure, as was indicated by the water manometer.

The trapped gas was compressed to about 10 psig by increasing the height of the mercury reservoir, thus forcing the gas into the lucite cylinder via line B. The residual volume left in the burette was measured and the volume of gas that had been forced into the cylinder was known by difference.

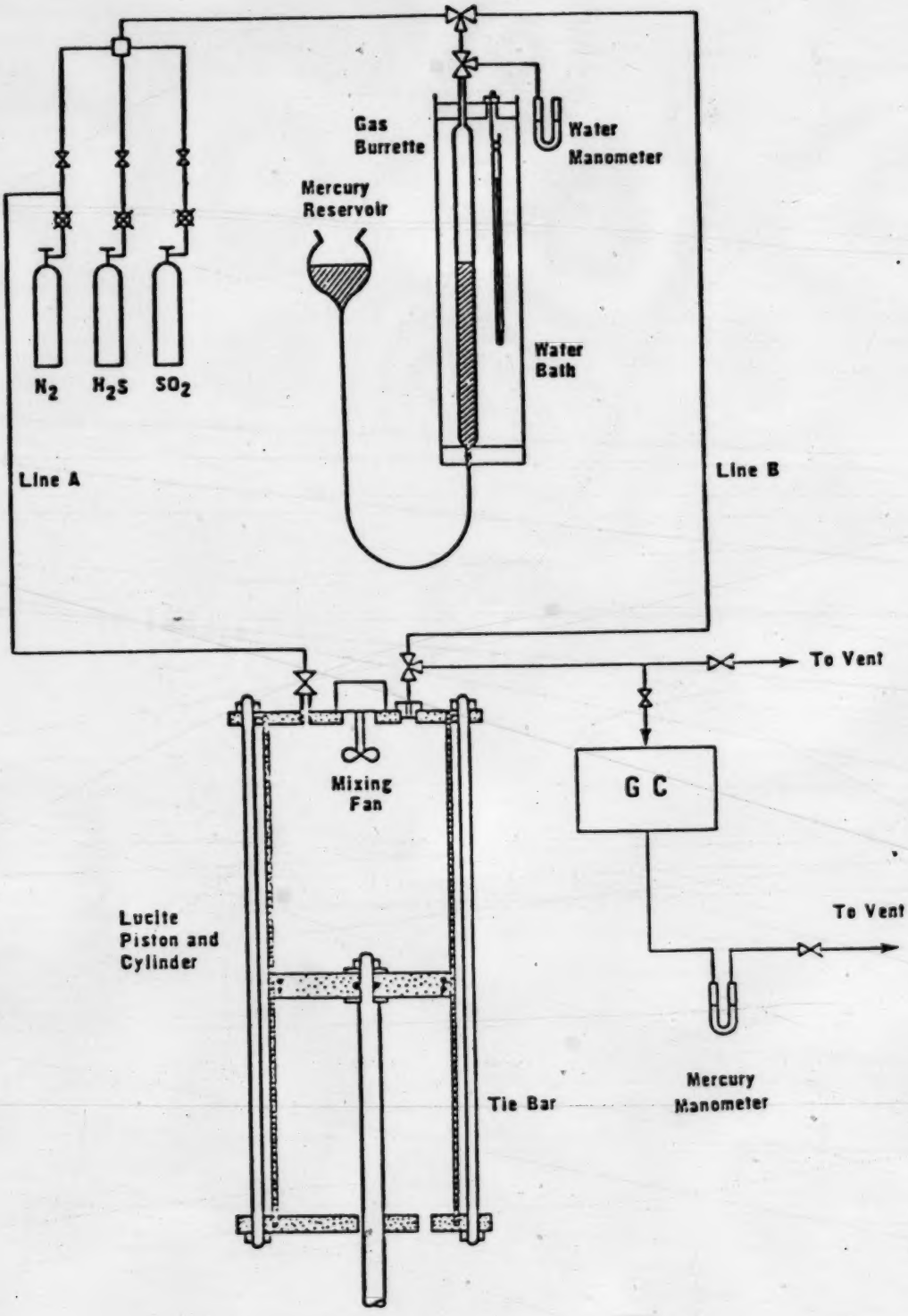


Figure A-1.2 G.C. Calibration Apparatus

The cylinder mixture was allowed to mix thoroughly using the fan for about 20 minutes. The gas was then forced through the G.C. sampling valve by raising the piston. Several samplings were taken of each mixture and the average peak areas calculated.

Since only small amounts of these two gases were expected in the product stream, all calibration mixtures were kept below 1%. The following Tables A-1.6 and 1.7 summarise the calibration data taken.

Calibration of the water peak area was somewhat different, since the above apparatus was useless for high water concentrations. The water syringe feeder that has been described above was used in conjunction with the nitrogen D/P cell to establish the G.C. water response factor. Using the syringe feeder and D/P calibrations, mixtures of known H_2O/N_2 composition were obtained. These were mixed using the reactor impeller and fed directly to the G.C. An attempt was made to calibrate the G.C. water reponse using gravimetric analysis using "Drierite" and molecular seive, however, the results were subject to large variations. The calibration data obtained are given below in Table A-1.8

The response factors for H_2S and SO_2 are constant. The response factor for H_2O is shown to be a function of the mol percent of water, since the intercept of the least squares straight line is much larger than zero. (0.09237). At small concentrations of water there would be a large error due to the assumption of a constant value for the response factor. The calibration has been performed over a greater range of water partial pressures than that to be encountered during the experimental runs, from less than 1% to greater than 14.5 . In order to minimise the effect of the variation in the response factor, the water peak calibration data were fitted using a quadratic equation. This data is contained in Table A-1.9. The mole fraction of water must now be obtained by an iterative technique. A response factor is assumed and the mole fraction calculated. The response factor is recalculated and the iteration is performed until the mol response factor converges. This procedure is described in more detail in Appendix 2.

Table A-1.2 Water Syringe Feeder Calibration, 1/1000 range

X = Percentage flow / 100

Y = Mass Flow, g/min * 100

The Coefficients of the Polynomial

$A_0 = -0.10665$

$A_1 = 0.45620$

Calibration Data

X measured	Y observed	Y calculated	PCT error
1.000	0.3624	0.34955	2.55
2.0000	0.78271	0.80575	2.94
4.0000	1.72394	1.71815	0.34
5.0000	2.17974	2.1744	0.25
6.0000	2.6178	2.63055	0.48
6.0000	3.1193	3.08678	1.04
8.0000	3.524	3.54295	0.55
9.0000	3.9973	3.99915	0.05

Variance = 0.000335

Standard Deviation = 0.018297

Maximum Pct Error = 3.548072

The calibration equation is therefore,

$$\text{mass flow (g/min)} = 4.5620 * 10^{-5} X(\text{percent flow}) - 0.10665 * 10^{-3} \quad \text{(A-1.1)}$$

Table A-1.3

Water Syringe Feeder Calibration, 1/100 range

X = Percentage flow / 100

Y = Mass Flow, g/min * 10

The Coefficients of the Polynomial

$A_0 = -0.09326$

$A_1 = 0.46653$

Calibration Data

X measured	Y observed	Y calculated	PCT error
0.5000	0.14293	0.14000	2.05065
1.0000	0.38800	0.37326	3.79855
2.0000	0.82693	0.83979	1.55478
3.0000	1.29130	1.30631	1.16246
4.0000	1.76930	1.77284	0.19987
5.0000	2.25310	2.23936	0.60977

Variance = 0.000164

Standard Deviation = 0.012788

Maximum Pct Error = 3.798551

The calibration equation is therefore,

$$\text{mass flow (g/min)} = 0.46653 * 10^{-3} \text{ X (percent flow)} - 0.009326 \qquad \text{(A-1.2)}$$

Table A-1.4 Calibration of Differential Pressure Cell

X = Chart Percent

Y = Flow Rate squared, $(l/min)^2$

The Coefficients of the Polynomial

$A_0 = -0.05350$

$A_1 = 0.08998$

Calibration Data

X measured	Y observed	Y calculated	PCT error
3.2500	0.22966	0.23895	4.04475
7.2500	0.59247	0.59889	1.08349
7.7500	0.63072	0.64388	2.08628
13.750	1.19806	1.18379	1.19155
18.500	1.64552	1.61121	2.08484
21.500	1.91421	1.88117	1.72629
22.000	1.89946	1.92616	1.40536
29.750	2.59748	2.62354	1.00325

Variance = 0.000595

Standard Deviation = 0.024393

Maximum Pct Error = 4.044746

The calibration equation is therefore,

$$Q\ (l^2/min) = 0.08998\ X\ (\text{chart percent}) - 0.05350 \quad \ldots\ldots\ldots\ (A-1.3)$$

Table A-1.5 Pressure Transducer Calibration

X = Chart Percent

Y = Pressure Cm Hg

The Coefficients of the Polynomial

$A_0 = 0.01383$

$A_1 = 0.89557$

Calibration Data

X measured	Y observed	Y calculated	PCT error
3.2500	3.00000	2.92444	2.51869
10.000	9.00000	8.96954	0.33841
32.000	28.4000	28.6721	0.95808
40.000	36.0000	35.8367	0.45374
60.750	54.4000	54.4198	0.03632
65.000	58.0000	58.2259	0.38955
70.500	63.4000	63.1517	0.39184

Variance = 0.036751

Standard Deviation = 0.191707

Maximum Pct Error = 2.518685

The calibration equation is therefore,

$$Pr\ (Cm\ Hg) = 0.89557\ X\ (chart\ percent) + 0.01383 \quad \ldots\ldots\ (A-1.4)$$

Table A-1.6 Calibration of Gas Chromatograph, Hydrogen sulphide

$X = (H_2S/N_2)area$

$Y = (H_2S/N_2)mol$

The Coefficients of the Polynomial

$A_0 = -0.00198$

$A_1 = 1.84419$

Calibration Data

X measured	Y observed	Y calculated	PCT error
0.06540	0.12840	0.11863	7.60692
0.08110	0.14860	0.14759	0.68208
0.08753	0.16290	0.15944	2.12118
0.09820	0.17500	0.17912	2.35547
0.15440	0.26990	0.28277	4.76669
0.16160	0.30210	0.29604	2.00482
0.16510	0.30430	0.30250	0.59215
0.26600	0.47700	0.48858	2.42695
0.29430	0.53690	0.54077	0.72026
0.41690	0.77720	0.76686	1.32986

Variance = 0.000065

Standard Deviation = 0.008073

Maximum Pct Error = 7.606923

The calibration equation is therefore,

Response Factor $H_2S = 1.84419$ . . . . . (A-1.5)

Table A-1.7 Calibration of Gas Chromatograph, Sulphur Dioxide

$X = (SO_2/N_2)$area

$Y = (SO_2/N_2)$mol

The Coefficients of the Polynomial

$A_0 = 0.00508$

$A_1 = 1.20770$

Calibration Data

X measured	Y observed	Y calculated	PCT error
0.09162	0.11260	0.11573	2.77797
0.12760	0.16820	0.15918	5.36201
0.14700	0.17250	0.18261	5.86116
0.20310	0.25660	0.25036	2.43080
0.25050	0.32172	0.30761	4.38058
0.25700	0.30920	0.31546	2.02384
0.27630	0.32810	0.33877	3.25093
0.37100	0.44870	0.45314	0.98856

Variance = 0.000079

Standard Deviation = 0.008881

Maximum Pct Error = 5.861156

The calibration equation is therefore,

Reponse Factor $SO_2 = 1.20770$ . . . . . (A-1.6)

Table A-1.8 Calibration of Gas Chromatograph, Water

$X = (H_2O/N_2)$area

$Y = (H_2O/N_2)$mol

The Coefficients of the Polynomial

$A_0 = 0.09237$

$A_1 = 1.04680$

Calibration Data

X measured	Y observed	Y calculated	PCT error
0.7648	0.86370	0.89296	3.2770
1.2280	1.32530	1.37248	3.43216
2.1471	2.21600	2.34005	5.29994
2.8680	2.93040	3.09460	5.30658
3.3325	3.46080	3.58200	3.38499
6.8273	7.50950	7.23924	3.37341
9.5966	10.9890	10.1381	8.19377
13.830	13.9340	14.5696	4.36255

Variance = 0.035997

Standard Deviation = 0.189729

Maximum Pct Error = 8.19377

The calibration equation is therefore,

Response Factor $H_2O = 1.0468$ ..... (A-1.7)

Table A-1.9 Water Response Factor Variation

X = mol % H_2O

Y = Response Factor, (H_2O/N_2)area / (H_2O/N_2)mol

The coefficients of the polynomial,

A0 = 0.87473

A1 = 0.01918

A2 = −0.00091

Calibration Data

X measured	Y observed	Y calculated	PCT error
0.75900	0.88550	0.88876	0.36826
1.20800	0.92281	0.89657	2.84383
1.80200	0.82810	0.90633	9.44654
2.78800	0.87870	0.92110	4.82561
3.62600	1.08715	0.93226	14.24710
6.39100	0.90910	0.95997	5.59573
9.43700	0.94822	0.97430	2.75076
12.15000	0.99250	0.97278	1.98731

Variance = 0.005181

Standard Deviation = 0.071976

Maximum Pct error = 14.2471

The calibration equation is therefore,

Response Factor $H_2O = 0.87473 + 0.01918\ (\text{mol\%}) - 0.00091\ (\text{mol\%})^2$ .... (A-1.8)

APPENDIX 2 Sample Calculations and Analysis

This Appendix begins with a definition of the names used to identify each of the variables necessary in the data-reduction. The experimental raw data from a single run is used to illustrate the application of the calibration data and the determination of the feed and reactor conditions. The establishment of the actual feed and reactor compositions is complicated by the fact that sulphur exists as a distribution of several different species. The derivation of the equations used to estimate the actual feed and reactor compositions will be given below and the iterative technique used to obtain the solution to these equations will be described in detail. The various kinetic parameters are then calculated.

There then follows the calculation used to obtain the volume of the reactor and the estimation of the validity of the assumption of ideal (gradientless) Berty reactor operation as developed by Kuchcinski and Squires.

Examples of the calculation of the rate constants are then given, followed by the calculation of the forward rate of reaction. Finally, the comparison of the two feasible sulphur species distributions is given.

Sample Calculations

The following calculation uses the experimental data obtained from the run WI01A. The calculation follows the scheme of the data analysis program EXPTCAL, which is listed in Appendix 3. The variables are subject to calibration, whose derivations can be found in Appendix 1.

In general, the variables can be identified by this key :

A = area	F = feed	G = mass flow
HO = water	HS = H_2S	N = N_2
P = pressure	R = reactor	RT = R * Temperature
S = sulphur	SO = SO_2	
V = volumetric flow	X = conversion	Z = molar flow rate

The raw data for run WI01A were :

Variable (name)	Exptl value
Weight of catalyst (WT)	0.6079 g
D/P cell chart % (DP)	1.64 %
Atmospheric Pressure (ATMP)	705.0 mm Hg
Feed Pressure (FP)	8.35 lbs/in^{2}g
Reactor Pressure (RP)	46.5 %
Feed Temperature (TF)	34.0 °C
Reactor Temperature (RT)	318.0 °C
Feed water area % (AWF)	1.2905
Sulphur feed rate (ZS1F)	0.0014937 mol/min
H_2S area % (AHSP)	0.10306
SO_2 area % (ASOP)	0.0883
H_2O area % (AWP)	1.1220
Volume of reactor (VR)	664 cm^3

The first step in the data analysis was to apply the calibration equations to the raw data and obtain the actual experimental conditions.

Convert temperatures to Kelvin ;

Feed Temperature, TF = TF + 273.15 = 307.15 K.

Reactor temperature, TR = TR +273.15 = 591.15 K.

Convert pressures to Newtons/metre^2

Atmospheric pressure, ATMP =ATMP * 101325/760 = 93922.3 N/m^2

Feed pressure, FP = (FP/14.17) * 101325 + ATMP = 149328.7 N/m^2

Apply calibration equation A-1.4 to obtain the reactor pressure

Reactor Pressure, RP = (0.89957*RP−0.32023)*101325/76.0 + ATMP

= 149264.1 N/m²

Volumetric flow of nitrogen, apply calibration equation A−1.3

VN = (0.14167 * DP − 0.096994) * 0.001 = 3.678924 * 10^{-4} m³/min

Calculation of N_2 flow from the ideal gas law,

molar flow N_2, ZN = FP * VN/(8.314*TF) = 2.182272 * 10^{-2} mol/min

To calculate the mol percentages of H_2S, SO_2 and H_2O in the product stream on a sulphur free basis, the response factors (RF) from the calibration equations A−1.7 to A−1.9 are applied :

RFHS = 1.92045

RFSO = 1.32023

RFHO = 0.87473 + 0.01918 WP − 0.00091 WP²

where WP = mol% water in G.C. product stream.

Then, mol% H_2S (HSP) = 100 * RFHS * AHSP / DEN

where,

DEN = (RFHS * AHSP + RFSO * ASDP + RFHO * AWP + 1.0 * (100−AHSP−ASDP−AWP)

Similarly, mol% SO_2 (SDP) = 100 * RFSD * ASDP / DEN

and,

mol% H_2O (AWP) = 100 * RFHO * AWP / DEN

Since the response factor for water is a function of the mol% of water, the following iterative procedure was performed.

1. Assume the value of RFHO, the water response factor
2. Calculate the mol% of H_2O, H_2S and SO_2.

3. From equation A−1.9, calculate the corresponding response factor.
4. Compare this response factor with the previous one, if they differ by more than $5 * 10^{-5}$, repeat steps 2 to 4 until RFHO converges.
5. Stop.

The mole percent of water in the feed (WF), is calculated from AWF by the same procedure, ie.,

$$\text{mol\% } H_2O \text{ feed} = 100 * RFHO * AWF / (RFHO * AWF * 1.0 * (100 - AWF)$$

Once again iteration is required to determine RFHO.

Following this procedure, the results that are obtained are :

For the feed,

RFHO =0.89576

WF = 1.15754

For the product,

RFHO = 0.893073

WP = 1.00200

HSP = 0.197155

SDP = 0.116572

The mol flow of water in the feed is therefore,

$$ZWF = WF * ZN / (100 - WF) = 2.13182 * 10^{-4} \text{ mol/min}$$

The total mass flow rate of the feed is,

$$GFT = ZN * 28 + ZWF * 18 + ZS1F * 32 = 0.561620 \text{ g/min}$$

This completes the preliminary calculations on the raw experimental data. The calculation of the flow rates of the product stream components is left until after the distribution of sulphur species is calculated.

Calculation of Feed Composition

Because sulphur vapour is an equilibrium distribution of several species, it is necessary to use an iterative technique to establish the actual mole fractions and mole numbers. The method used in this work was developed by Razzaghi (74).

Only the sulphur species S_2, S_4, S_6 and S_8 have been included, since these species are most likely to be present and since there is no definitive data on the equilibrium composition of sulphur vapour. The data available on the even numbered species are the most reliable (74).

Assuming the sulphur vapour to be at equilibrium, the Claus process consists of the following set of reactions :

$$2\,H_2S + SO_2 \rightleftharpoons 3/8\,S_8 + 2\,H_2O \qquad K1$$

$$S_8 \rightleftharpoons 4\,S_2 \qquad K2$$

$$S_8 \rightleftharpoons 2\,S_4 \qquad K4$$

$$S_8 \rightleftharpoons 4/3\,S_6 \qquad K6$$

The Ki are the equilibrium constants of each reaction. These reactions form a consistent set of non-redundant reactions and are used to calculate the thermodynamic equilibrium of the Claus reaction.

From thermodynamics, $K_1 = \exp(-\Delta G^0/RT)$, hence the the equilibrium constants of these reactions can be calculated from the Gibbs free energy data on the species in the reaction system. For any system at equilibrium, the Gibbs free energy is a minimum, and since the equilibria of the above reactions can also be calculated in terms of the partial pressures of the species, there is a system of equations which can be solved, and the equilibrium mole fractions of the species obtained.

The mass balances on the total mixture and on the sulphur component form two equations in several unknowns. However, applying the constraints imposed by stoichiometry and thermodynamics, the number of unknowns can be reduced to only two. This is a pair of non-linear equations in two unknowns, therefore they may be solved by a suitable iterative technique. The derivation of these equations and the method of their solution employed in this work, is given below.

Assume unit mole of inlet gas, composition Yw, Yn_2, Ys_1

Let X be the conversion of H_2O at any time.

From a mass balance, the following equations are derived :

$$Y^1w = Yw - X\,Yw$$

$$Y^1n_2 = Yn_2$$

$$Y^1h_2s = X\,Yw$$

$$Y^1so_2 = \tfrac{1}{2}\,X\,Yw$$

$$Y^1s_2 = a_2$$

$$Y^1s_4 = a_4$$

$$Y^1s_6 = a_6$$

$$Y^1s_8 = a_8$$

where (^{1}) denotes products, and the a's are the unknown amounts of the sulphur species present in the product. Total moles (Nt), in the product, is therefore,

$$Nt = Yw + Yn_2 + \tfrac{1}{2}\,X\,Yw + a_2 + a_4 + a_6 + a_8 \qquad \text{..... (A-2.1)}$$

Performing a mass balance on the sulphur species,

$$Sin = 8\,Ys_1$$

$$Sout = X\,Yw + \tfrac{1}{2}\,X\,Yw + 2\,a_2 + 4\,a_4 + 6\,a_6 + 8\,a_8$$

$$8\,Ys_1 = X\,Yw + \tfrac{1}{2}\,X\,Yw + 2\,a_2 + 4\,a_4 + 6\,a_6 + 8\,a_8 \qquad \text{..... (A-2.2)}$$

For ideal gases, $Keq. = Kp = \sum P^1i / \sum Pi$

where Pi = the partial pressure of species i.

$$\Longrightarrow K2 = \frac{a_2^4 * Nt^3}{a_8 * P^3} \qquad \longrightarrow a_2 = \left\{ \frac{K2 * a_8 P^3}{Nt^3} \right\}^{0.25} \qquad \text{..... (A-2.3)}$$

$$\Longrightarrow K4 = \frac{a_4^2 * Nt}{a_8 * P} \qquad \longrightarrow a_4 = \left\{ \frac{K4 * a_8 P}{Nt} \right\}^{0.50} \qquad \text{..... (A-2.4)}$$

$$\Longrightarrow K6 = \frac{a_6^{1.33} * Nt^{0.33}}{a_8 P^{0.33}} \qquad \longrightarrow a_6 = \left\{ \frac{K6 * a_8 P^{0.33}}{Nt^{0.33}} \right\}^{0.75} \qquad \text{..... (A-2.5)}$$

substituting (A-2.3) (A-2.4) and (A-2.5) into (A-2.2),

$$8\,Ys_s = 3/2\ X\ Yw + 2\,(K2\,a_s\,P^3)^{0.25} + 4\,(K4\,a_s\,P)^{0.5} + 6\,(K6\,a_s\,P^{0.33})^{0.75} + 8\,a_s$$
$$Nt^3 \qquad\qquad Nt \qquad\qquad Nt^{0.33} \qquad\qquad \text{(A-2.6)}$$

This equation is a function of two variables only, a_s and Nt. Let,

$$A = (K2\,P^3)^{0.25},$$

$$B = (K4\,P)^{0.5}$$

$$C = (K6\,P^{0.33})^{0.75}$$

then substituting in A-2.5 and rearranging, the following function is obtained,

$$F_1(\Phi) = (3/2\ X\ Yw\ Nt^{0.75}) + (2\ A\ a_s^{0.5}) + (4\ B\ a_s^{0.5}\ Nt^{0.25}) + (6\ C\ a_s^{0.75}\ Nt^{0.5})$$
$$+ (8\ (a_s - Ys_s)\ Nt^{0.75}) = 0 \qquad \text{(A-2.7)}$$

substituting similarly in (A-2.1),

$$F_2(\Phi) = Nt^{1.75} - Nt^{0.75}\ (Yw + Yn_2 + \tfrac{1}{2}\ X\ Yw) - A\ a_s - B\ a_s\ Nt^{0.25} - C\ a_s\ Nt^{0.5}$$
$$+ a_s\ Nt^{0.75} = 0 \qquad \text{(A-2.8)}$$

==> two non-linear equations in two unknowns.

The Newton-Raphson technique is used to obtain the solution. This method requires the Jacobian matrix, and hence the partial derivatives of the equations must be evaluated.

These are found by straightforwardly differentiating equations A-2.6 and A-2.7 above, viz.

$$\partial f_1 / \partial\, a_s = A\ a_s^{-0.75} + 2\ B\ a_s^{-0.5}\ Nt^{0.25} + 4.5\ C\ a_s^{-0.25}\ Nt^{0.5} + 8\ Nt^{0.75} \qquad \text{(A-2.9)}$$

$$\partial f_1/\partial Nt = 1.125 \times Yw\, Nt^{0.25} + 0 + B\, a_s^{0.5}\, Nt^{-0.75} + 3\, C\, a_s^{0.75}\, Nt^{-0.5} + 6\, Nt^{-0.25}(a_s - Ys_s) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (A-2.10)$$

$$\partial f_2/\partial a_s = 0 - 0 - A - B\, Nt^{0.25} - C\, Nt^{0.5} + a_s\, Nt^{0.75} \quad \ldots\ldots\ldots\ldots\ldots (A-2.11)$$

$$\partial f_3/\partial Nt = 1.75\, Nt^{0.75} - 0.75\, Nt^{-0.25}(Yw + Yn_2 + \tfrac{1}{2} \times Yw) - 0 - 0.25\, B\, a_s\, Nt^{-0.75} + C\, a_s\, Nt^{-0.5} + 0.75\, a_s\, Nt^{-0.75} \quad \ldots\ldots\ldots\ldots\ldots (A-2.12)$$

To solve equations A-2.6 and A-2.7 for Nt and a_s, the constants in these equations must be evaluated and so the equilibrium constants K1, K2, K4, K6, must first be calculated. These are obtained from the Gibbs free energy of the species. The Gibbs free energy of each species is calculated using the standard free energies and specific heat data as given by Rau(71), in the case of the sulphur species, and JANAF (36) for the others. The Gibbs free energy of each species is calculated from the relationship :

$$G = a * (1.0 - \log T) - 1/2\, b\, T - 1/6\, c\, T^2 - 1/12\, d\, T^3 - 1/20\, e\, T^4 + f/T - g - h/T^2$$

where T = temperature in Kelvin, and the constants a to h are the empirical constants of the specific heat polynomials as given by Rau and in JANAF. The derivation of the above relationship may be found in the CRC handbook (14) (page D-61).

For H_2S,

$$Gh_2s = 3.9163 * (1 - \log(593)) + 3.5138 * 10^{-4}\, 593/2 - 4.21913 * 10^{-6}\, 593^2/6 + 2.7454 * 10^{-9}\, 593^3/12 - 4.8583^{-13} * 593^4/20 - 3609./6/593 - 2.366 - 0$$

$$Gh_2s = -29.6403$$

Similarly,

$$Gso_2 = -91.00975$$

$Gh_2o = -72.51437$

$Gs_2 = -2.039625$

$Gs_4 = -9.48614$

$Gs_6 = -25.38013$

$Gs_8 = -35.30612$

The changes in the free energy are calculated for each reaction. For example

$$4S_2 \longrightarrow S_8$$

$$\Delta G = 4 \quad Gs_2 - \quad Gs_8$$

Thus, $G = -2.039625 * 4 + 35.30612 = 27.14762$ (= DFRT2)

Similarly,

DFRT4 = 16.338

DFRT6 = 1.46596

DFRT81 = 7.97693

The equilibrium constants are then calculated from the following equation,

$$K2 = \exp(-DFRT2/RT)$$

Thus, $K2 = 1.621571 * 10^{-11}$

$K4 = 8.0593723 * 10^{-8}$

K6 = 0.2308563

$K81 = 3.4329075 * 10^{-4}$

The feed composition can now be calculated using multiple iterations.

The mole fractions of hydrogen sulphide and sulphur dioxide in the feed are zero. The mole fractions of nitrogen and water are estimated assuming the sulphur to be entirely S_8. The total mole fraction is assumed to be 1.0. For the case of the feed, the conversion is 0.0. The assumption, as a first estimate, that the feed consists entirely of S_8 allows the calculation of the feed molar flow rate,

total feed moles, ZFT= ZN + ZWF + ZS1F/8.0 = 0.01860356 mol/min

The initial mole fractions can now be calculated,

YW = ZWF/ZFT = 0.01145918

YS8 = ZS1F/8.0/ZFT = 0.01993638

YN = ZN/ZFT = 0.9785044

The subroutine NLSYST is called, having first determined the various constant inputs required, A, B, and C. The other constants D and E are required but both of these are functions of the water and nitrogen mole fractions and are subject to change as the correct mole fractions of S_8 is obtained.

Operation of NLSYST

The two functions and their partial derivatives are evaluated using the first guess estimates. An external subroutine LEQT1F is called from the IMSL program library to solve for the roots of the functions. The subroutine obtains the solution of the set of linear equations,

$$A\,X = B$$

Matrix A contains the Jacobian matrix and hence this scheme follows the Newton Raphson iterative technique where,

$$x_2 = x_1 - f_1(x)/f_1^1(x)$$

The system of equations is solved repeatedly until f_1 and $f_2 = 0$, to within 10^{-9}.

The functions are re-evaluated and when the value of each is within a certain tolerance, the routine returns to the main program with the new estimates of Nt and Ys_8.

The mole fractions of every species are now calculated using equations (2.2) (2.3) and (2.4).

$$mf\ S_8 = [K6\ Ys_8 * P^{0.33}/Nt^{0.33}]^{0.75}$$

The partial pressures and mass flow rates of each component are calculated :

PPi = mfi * Press(atm) * 101325(N/m²/atm)

GFi = mfi *MWi * ZFT, the total mole flow rate

The actual sulphur feed mass flow rate is calculated :

$$SGFA = ZS1F * 32.0 \text{ g/min}$$

and the sulphur feed mass flow rate is calculated,

$$SGF = SGFi$$

The constants D and E contain the initial values of YN YW and YS8. and so the Newton Raphson technique must be re-applied using the new estimates of the mole fractions. Two tests are therefore performed to test for overall convergence.

1. The total mole fraction is evaluated. Since unit mole of feed has been assumed, the total mole fraction will converge to 1.0. The actual mole feed is adjusted according to the component mol fraction, viz.

$$ZFT_2 = ZFT_1 * TFMF \text{ (total mol fraction feed)}$$

The mole fractions are now recalculated using this new estimate of the total mole feed rate.

2. The mass balance on sulphur is evaluated in order to obtain a new estimate of YS8, viz.,

$$(YS8)_2 = SGFA/SGF * (YS8)_1 = \text{actual mass flow S/ calculated mass flow}$$

The constants D and E can now be recalculated and the routine NLSYST is called repeatedly until both TFMF and SGFA/SGF = 1.0.

Calculation of actual flows

The feed composition and the relative amounts of the various sulphur species are obtained in this manner.

The volumetric feed flow is calculated from the ideal gas law,

$$VFT = ZFT * RT/RP$$

Before the rate of reaction can be determined, the distribution of sulphur species for the reactor conditions must be calculated. This is done in a similar manner to the feed composition, only in this case the conversion does not equal 0.

ZN = as before

ZWP = WP * ZN/(100 - WP)

Therefore, conversion = (ZWF - ZWP)/ZWF

The initial guess to be fed to NLSYST is calculated. The total moles is again assumed to be 1.0. The mole fractions of nitrogen and water are calculated again assuming all the sulphur is in the S_8 form.

Total product moles = ZN + ZWP+ZS1F/8.0 *(1.0 - 3/16 X)

--> YN = ZN/ZPT

YW = ZWP/ZPT YS8 = ZS1F/8.0 * (1.0 - 3/16 X)/ZPT

This initial estimate of the variables is passed to the iteration loop and the solution is obtained as in the case of the feed composition.

The volumetric flow is calculated from the ideal gas law :

VPT = ZPT * RT/RP

The atom balances on each of the elements are calculated, for Hydrogen for example,

AHF = mf H_2O feed * ZFT * 2.0

AHP = mf H_2O product * mf H_2S product * ZPT* 2.0

Evaluation of kinetic variables

The various kinetic variables can now be evaluated,

Residence time, =0.001 * Volume of the reactor/(volumetric flow prod. *60) s

Space velocity -> sv = 1/t

Conversion of water, as before, = (ZWF-ZWP)/ZWF

Conversion of sulphur 8, = (MF S_8*ZFT - MF S_8p * ZPT) /(MF S_8f * ZFT)

Water rate of reaction, = (ZWF - ZWP)/WT mol/s g cat

Sulphur rate of reaction = (MF S_8 * ZFT - MF S_8p * ZPT)/ WT mol/s g cat.

X - axis of initial rate plots = WFS = WT/(MF S_8 * ZFT * 60)

WFW = WT/(ZWF * 60.0) g mol/hr

The remainder of the program deals with printing the output.

Berty Reactor Ideal Operation

The set of equations derived by Kuchcinski and Squires were developed using a reactor similar to the one used in this work. They caution that the constants of these equations will be different for other Berty reactor configurations. However, since they used an Autoclave reactor it is probable that these equations are applicable to the reactor used in this study.

For Reynold's number < 50, the following equations apply,

$$\Delta T = 112\, r\rho\, \Delta H\, Pr^{2/3}\, (T/M\,P)^{1/2}\, (1500/rpm)^{1/2}\, (4/(L/Dp))^{1/4} /$$
$$[Cp\,(a\psi)^{1.5}\,(\mu)^{0.5} \quad \ldots\ldots\ldots\ldots (6.1)$$

$$\Delta X = 47000\, r\rho\nu\, (T/P)^{1.16} /$$
$$[(a\psi)^{1.5}\,(Dim)^{0.67}\,(M/\mu)^{0.16}\,(rpm/1500)^{0.5}\,(4\,Dp/L)^{0.25}]$$
$$\ldots\ldots\ldots\ldots (6.2)$$

Slightly different equations are applied for Re > 50. For this reaction,

M = 29	a = 6/D = 1890
P = 1.5 * 10^5 Pa	ψ = 1
T = 600 K	μ = 3 * 10^{-5} Kg/ms
rpm = 1200	L/Dp = 1
$r\rho$ = 6.67 * 10^{-5} kg mol/s	ν = 1
$(a.\psi)$ = 1890 m^2 / m^3(bed)	Dim = 1.3 * 10^{-4}
H = 10^8 J/kmol	Pr = 0.68
Cp = 1000	

Substituting in the equations —>

Re = 16.8

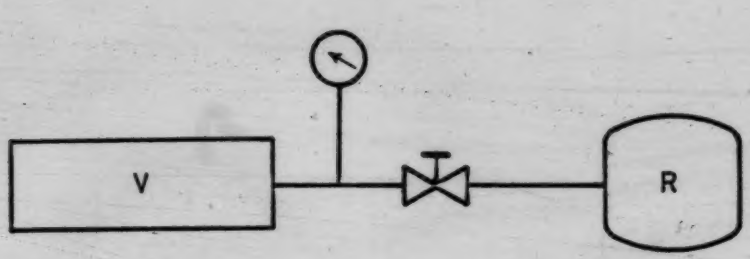
X = 4.87 * 10^{-4}

T = 2.00 * 10^{-2} K

Calculation of Reactor Volume

The volume of the reactor was determined by experiment in the following manner. A large vessel of known volume was connected to the the sealed reactor via a valve. A pressure gauge was inserted to measure the pressure as shown in Figure A-2.1.

Figure A-2.1 Measurement of Reactor Volume



The large vessel was pressurised using the building compressed air system to about 70 psig and connected to the reactor as shown. The pressures in the vessel and the reactor were recorded, the reactor pressure being assumed to be the same as atmospheric. The valve was then opened slightly, to allow the gas to flow slowly into the reactor, and the pressure was allowed to equilibriate. This final pressure was then recorded. The following assumptions allow this process to be used to calculate the volume of the reactor. The air is assumed to behave as an ideal gas, and the process is isothermal. The volume of the reactor can be obtained viz.

Conditions for vessel 1, P_1, V_1 and n_1

Conditions for the reactor, P_2 V_2 and n_2. Let (^{1}) denote final conditions.

Applying the ideal gas law,

$$P_1 V_1/n_1 = P_2 V_2/n_2 = R T$$

now,

$$n^1 = n_1 + n_2 \text{ and } V^1 = V_1 + V_2$$

$$\longrightarrow P^1 (V_1 + V_2)/(n_1 + n_2) = P_1 V_1/n_1$$

and,

$$n_2 = (P_2 V_2/P_1 V_1)\, n_1$$

$$\longrightarrow P^1(V_1 + V_2)/(n_1[1 + P_2 V_2/P_1 V_1] = P_1 V_1/n_1$$

which on rearranging yields,

$$V_2 = V_1(P^1 - P_1)/(P_2 - P^1)$$

The volume of vessel 1 was 500 in^3, atmospheric pressure was 700 mmHg and temperature was 25 °C.

Calculation of Rate Constants

Equation 5.2 is the model which has been fitted to the initial rate data,

$$-Rw\ 10 = a\,(Pw/10^4)^b\ /(1 + c\,(Pw/10^4)^n)$$

With n=2, the parameters a, b, and c have the values, 0.3358, 0.8911 and 0.2740 respectively.

Thus,

$$-Rw = (Pw/10^4)^{0.89}\ 0.3358/(\ 10\ (1 + 2.74\ *10^{-5}\ Pw)^2)$$

$$-Rw = 9.1555 * 10^{-6}\ Pw\ /\ (1 + 2.74 * 10^{-5}\ Pw)^2$$

then,

$$k = 9.1555 * 10^{-6}/(Ps_p)^{0.89}$$

Since Ps_1 = 753 N/m², and the order with respect to sulphur is 0.39,

$$k = 9.1555 * 10^{-6}/(753)^{0.39} = 6.4606 * 10^{-7}$$

This will equal the least squares value of the rate constant since it is derived from the least squares fit to the model.

The rate constant may be calculated directly from the each initial rate viz.,

$$k = -Rw\,(1 + K\,Pw)^3/\,(Pw)^{0.39}\,Ps_1^{0.39})$$

$$= 1.904 * 10^{-2}(1 + 2.74 * 10^{-5}\,8204)^3/\,(8204^{0.39}\,753^{0.39})$$

$$= 7.0154 * 10^{-7}$$

Comparison of Forward and Reverse Reaction Rates

From Table 5.8, the initial rate of the reverse reaction at a partial pressure of 8204 N/m² water and 753 N/m² sulphur, and a temperature of 592 K, is 0.01904 mol/g hr.

Using equation 2.2, the rate of the forward reaction is given as,

$$-Rh_2s = 1.121\,\exp(-7440/RT)\,(61.5)\,(5.6)^{0.5}/\,(\,1 + 0.00423\,61.5)^3$$

$$= 0.17995$$

Thus the forward reaction is 9.75 times the rate of the reverse reaction.

Comparison of Sulphur Species Distributions

At a temperature of 592 K, and a pressure of 1.46 atmospheres and a mole percentage of sulphur of 0.388, the distributions of the sulphur species that are predicted from the thermodynamic data are as follows,

Species	mol % (8)	mol % (even)
S_1	0.0	
S_2	3.03	5.74
S_3	0.44	
S_4	0.26	0.27
S_5	3.35	
S_6	36.44	60.06
S_7	21.10	
S_8	35.4	35.93

The distributions are very similar although that which includes only the even species has an average molecule size which is slightly smaller, 6.4 as opposed to 6.7 for the complete distribution.

APPENDIX 3 Computer Programs

This Appendix contains listings of the computer programs used in the analysis of the experimental data. There are three main programs, EXPTCAL IRANAL and ADSREG, each of which uses a subroutine. The subroutine NLSYST is employed by EXPTCAL, and the subroutine NLREG is used by both IRANAL and ADSREG.

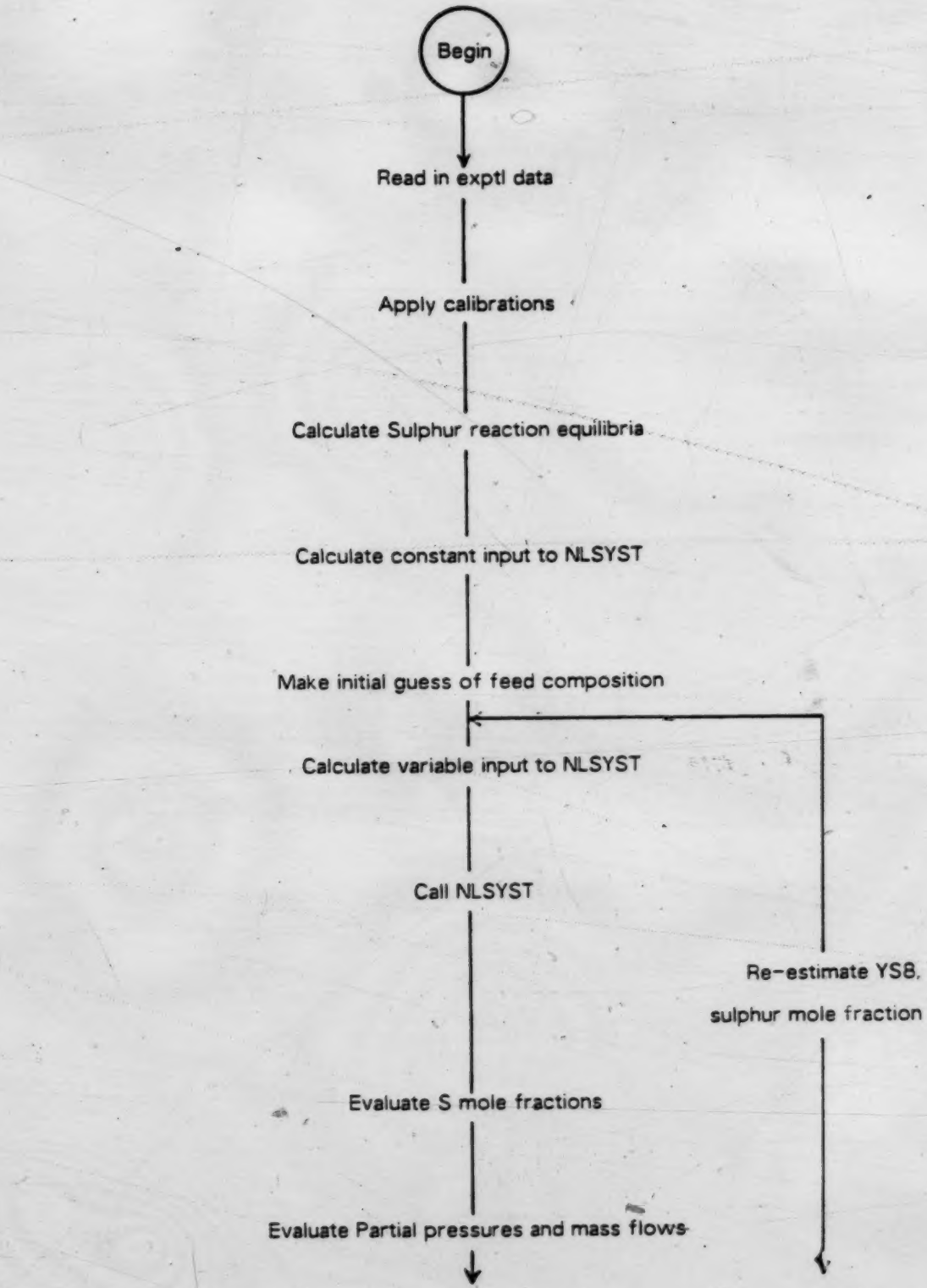
The raw data analysis and kinetic data calculation were performed by the FORTRAN computer program EXPTCAL (for EXPerimenTal CALculations). The calculations performed by this program have been illustrated in Appendix 2. The basic outline of the program is shown by the flow diagram below.

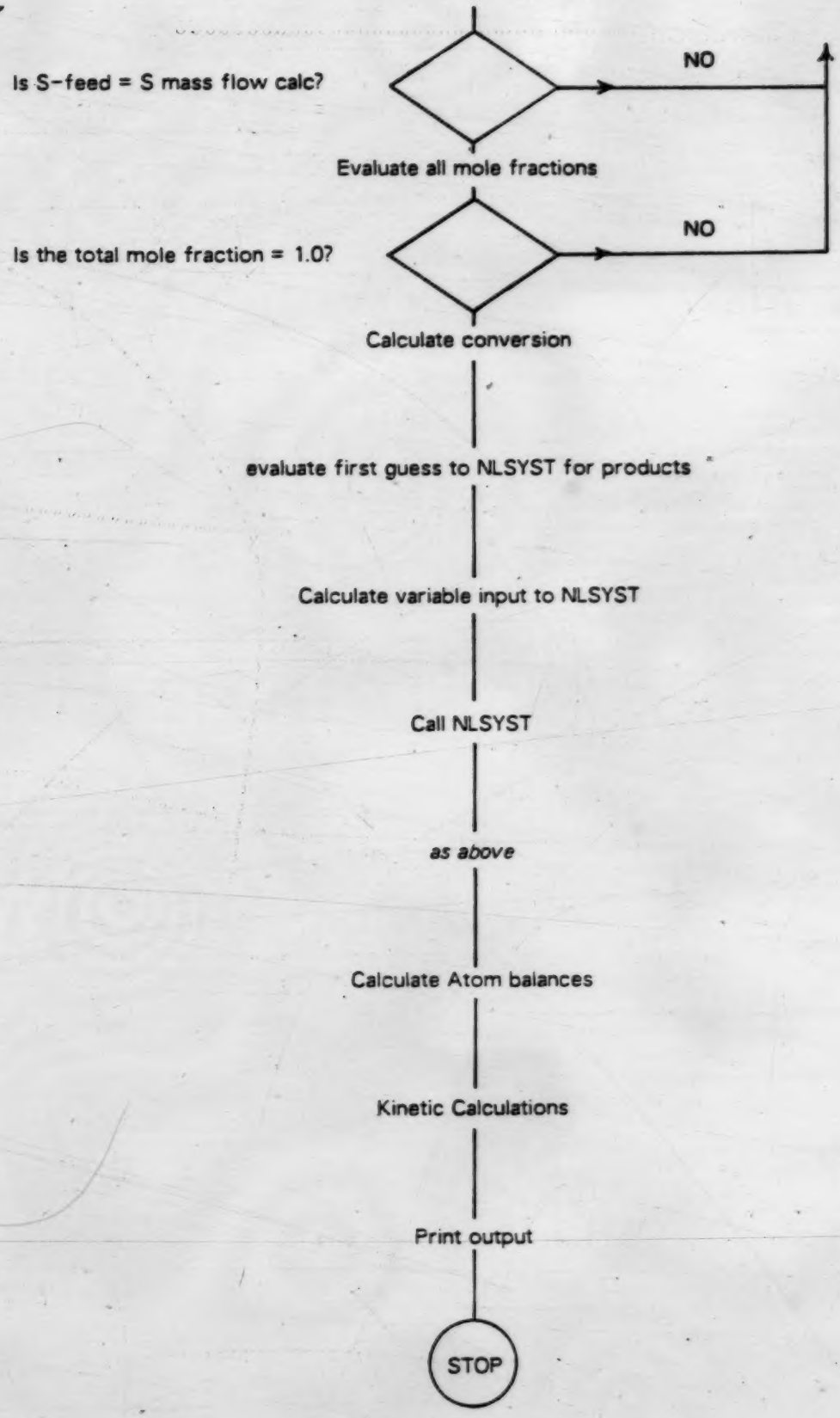
EXPTCAL employs a subroutine NLSYST (for Non-Linear SYSTem). This routine solves the non-linear pair of equations in Nt, the total mole fraction and Ys_1, the sulphur mole fraction using the Newton-Raphson technique. A flow chart outlining the main sections of this subroutine is given. NLSYST calls a subroutine LEQT1F from the IMSL (International Mathematical and Statistical Library). This routine solves a linear system of equations of the form, A X = B. The values of the kinetic variables of interest are calculated by EXPTCAL. A full listing of the output from this program can be found in Appendix 4.

The main program IRANAL (for Initial Rate ANALysis), sets up the non-linear curve fitting subroutine NLREG (Non-Linear REGression). IRANAL calculates the form of the function being fitted and its derivatives. The important features of this program and its subroutine are elaborated on below.

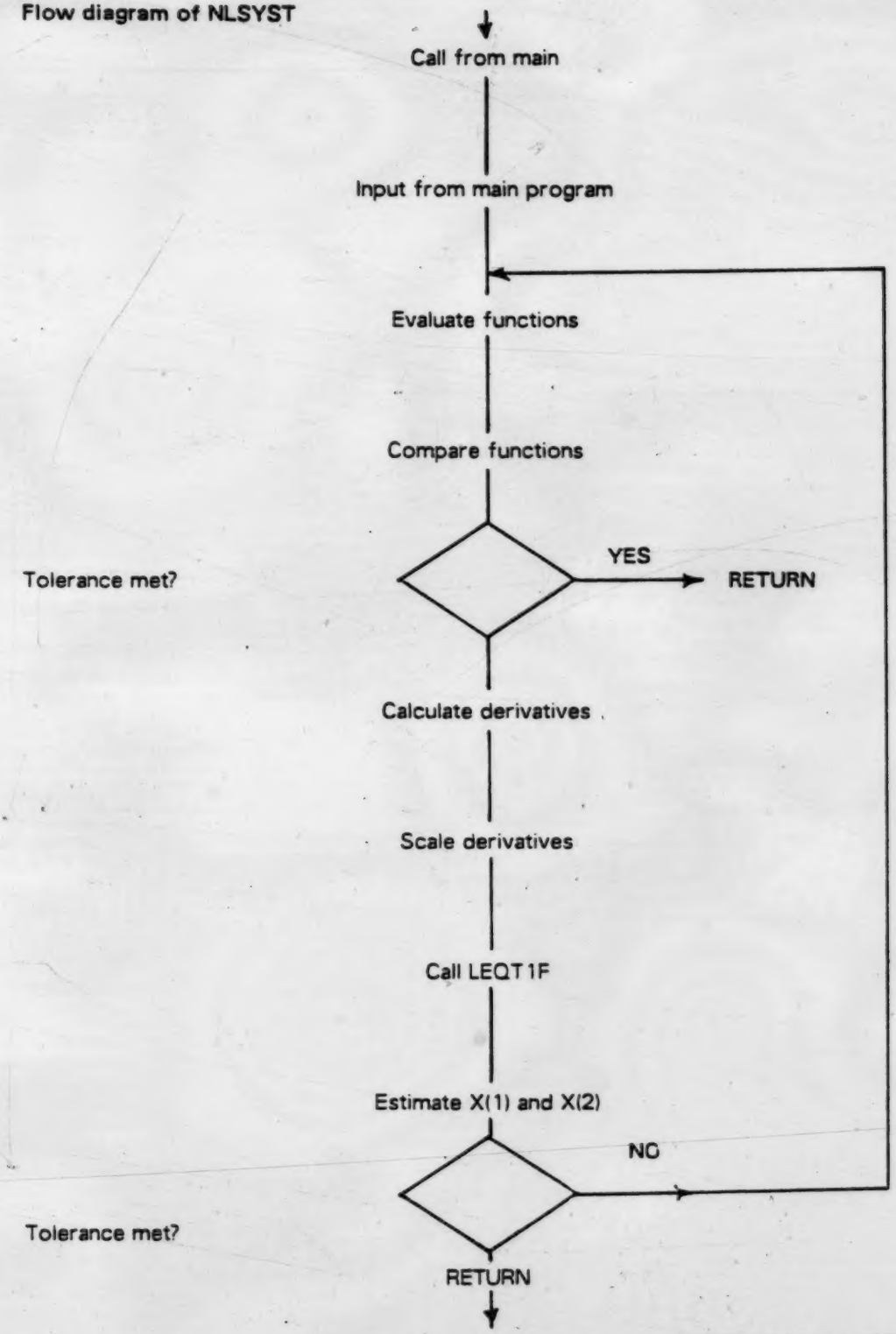
The main program ADSREG, (ADSorption REGression), fits the water rate function to the data using the subroutine NLREG. Several versions of this program were used depending on the power of the denominator term in the model.

Flow Chart of EXPTCAL




Is S-feed = S mass flow calc?
NO
Evaluate all mole fractions
Is the total mole fraction = 1.0?
NO
Calculate conversion
evaluate first guess to NLSYST for products
Calculate variable input to NLSYST
Call NLSYST
as above
Calculate Atom balances
Kinetic Calculations
Print output
STOP

Flow diagram of NLSYST



```
      C
C*************************************************
C
C              EXPTCAL
C
C       Experimental Calculations
C
C*************************************************
C
C MAIN PROGRAM FOR EXPERIMENTAL ANALYSIS
C FEED ASSUMED TO CONSIST OF N2, H2O AND S8
C CLAUS REACTION :- 2.H2S + SO2 <=> 2.H2O + 3/8.S8  81
C                        4.S2 <=> S8                28
C                        2.S4 <=> S8                48
C                      4/3.S6 <=> S8                68
C
C INPUT TO THIS PROGRAM SHOULD BE IN THIS
C FORM :-
C       NREP, NO OF COPIES OF OUTPUT REQUIRED
C       IREP, TERMINATION CODE, NEGATIVE IF NO
C             MORE DATA
C       RUNDAT(I),  STRING WHOSE FIRST FIVE MEMBERS
C             ARE THE RUN NUMBER FOLLOWED BY THE
C             DATE IN THE FORM 02/04/66.
C       WT IS THE WEIGHT OF CATALYST USED
C       RPM IS THE IMPELLER SPEED
C       DP IS THE D/P CELL CHART READING %
C       ATMP IS THE ATMOSPHERIC PRESSURE IN MM.HG
C       FP IS THE FEED PRESSURE IN PSIG
C       RP IS THE REACTOR PRESSURE IN CHART %
C       TF IS THE FEED TEMEPERATURE IN CELSIUS
C       TR IS THE REACTOR TEMPERATURE IN CELSIUS
C       AWF IS THE AREA % OF WATER IN THE FEED
C       ZS1F IS THE GM-ATOM FLOW OF SULPHUR FEED
C       AHSP, ASOP, AWP ARE THE AREA %'S OF
C           H2S, SO2 AND WATER RESPECTIVELY
C           IN THE PRODUCTS
C       THE DATA REQUIRED FOR THE CALCULATION OF
C           THE SULPHUR SPECIES EQUILIBRIA ARE READ
C           FROM UNIT 7 WHICH IS ATTACHED TO THE
C           GEN1, A LISTING OF WHICH IS GIVEN
C           FOLLOWING THIS ONE
C*************************************************************
C
C
      IMPLICIT REAL*8(A-H,O-Z,$)
      DIMENSION X(2),FRAC(7),F(2,1),ISPN(7),SNAM(7),FRE(7,8)
     #,FMF(8),EMF(8),FPP(8),EPP(8),GF(8),GP(8),CHEM(8),WMOL(8)
     #,RUNDAT(16),FRT(7)
       DATA CHEM/'N2  ','H2O ','H2S ','SO2 ','S2  ','S4  ',
     &'S6  ','S8  '/
       DATA WMOL/28.01,18.02,34.08,64.06,64.13,128.26,
     &192.38,256.51/
C
```

```
C      GIBB'S FREE ENERGY DATA INPUT
C
      ISPN(1)=7
      ISPN(2)=8
      ISPN(3)=6
      ISPN(4)=13
      ISPN(5)=15
      ISPN(6)=17
      ISPN(7)=19
      DO 10 I=1,7
      LINE=(ISPN(I)*4-3)*1000
      READ(7'LINE,40) SNAM(I)
40    FORMAT(A4)
      READ(7,41) (FRE(I,K) , K=1,4)
41    FORMAT(/,4E15.7)
      READ(7,42) (FRE(I,K) ,K=5,8)
42    FORMAT(4E15.7)
10    CONTINUE
C
C       EXPERIMENTAL DATA INPUT
C
       A0=0.87473
       A1=0.01918
       A2=-0.00091
       A02=1.15950
       A12=0.00227
       A22=0.00106
       RFHS=1.92045
       RFSD=1.32023
       RFHS2=1.84419
       RFSD2=1.20770
       DATA S /'S'/
       ITA=0
       ICT=5
       ICU=4
       WRITE(9,7)
7      FORMAT('$**$FONT=1200.BOLD.9.FIXED.LANDSCAPE.1',/,'1',
     & /,'4',60X,'RAW DATA TABLES',/,'+',60X,'RAW DATA
     & TABLES',/////,45X,'Wt.Cat.- units are Grammes',
     & //,45X,'RPM  - impeller speed, Revs per Minute',
     & //,45X,'D/P  - differential pressure cell
     & reading, Chart Percent',
     & //,45X,'ATMP - atmospheric pressure, mmHg',
     & //,45X,'FP   - feed pressure, psig',
     & //,45X,'RP   - reactor pressure transducer reading,  ',
     & 'Chart Percent',
     & //,45X,'TF   - feed nitrogen temperature, Celsius',
     & //,45X,'TP   - reactor temperature, Celsius',
     & //,45X,'AWF  - Area Percent water in feed',
     & //,45X,'ZS1F - mol flow S1 feed, Mol/Hr',
     & //,45X,'AHSP - Area Percent H2S in product,
     & sulphur free basis',
     & //,45X,'ASDP - Area Percent SO2 in product,
     & sulphur free basis',
```

```
     & //,45X,'AWP  - Area Percent water product, sulphur',
     & 'free basis',/)
       READ(5,12) NREP
12     FORMAT (I1)
13     READ(5,14) IREP
       IF(IREP.LT.0) GOTO 28
14     FORMAT(I2)
       READ(5,2) (RUNDAT(I),I=1,16)
2      FORMAT(16A1)
       READ(5,15 ) WT,RPM
15     FORMAT(F8.4,F6.0)
       READ(5,4) DP,ATMP,FP,RP,TF,TR
4      FORMAT(F6.2,F6.1,2F6.2,2F7.2)
       READ(5,6) AWF,ZS1F
6      FORMAT(F8.4,F10.7)
       READ(5,8)AHSP,ASDP,AWP
8      FORMAT(3F8.4)
       ICT=ICT+1
       IF(ICT.NE.6)GOTO 3
       IC=6
       IPAGE=1
       ICT=0
       GOTO 5
3      IC=0
       IPAGE=0
5      WRITE(9,1) IPAGE,IC,(RUNDAT(I),I=1,16),WT,RPM,DP,
     & ATMP,FP,RP,TF,TR,AWF,ZS1F,AHSP,ASDP,AWP
1      FORMAT(I1,/,I1,
     & 12X,' RUN',5X,'DATE',4X,'Wt.Cat.',3X,'RPM',
     & 4X,'D/P',4X,'ATMP',3X,'FP',4X,'RP',5X,'TF',5X,'TR',
     & /,13X,16A1,F8.4,F7.0,F7.2,F8.2,F6.2,F7.2,F7.2,F8.2,
     & /,13X,'AWF',6X,'ZS1F',7X,'AHSP',5X,'ASDP',5X,'AWP',
     & /,12X,F8.4,F11.7,F9.5,F9.5,F9.4,/)
C
C      END OF INPUT
C
C      FEED VARIABLE MANIPULATION
C
       VR=664.0
       TF=273.15 + TF
       TR=273.15+TR
       RT=8.314*TR
       ATMP= ATMP*101325/760
       FP=FP*6895+ATMP
       RP=(0.89557*RP-0.1383)*101325/76.0+ATMP
       VN=DSQRT(0.08998*DP-0.05350)*0.001
       ZN=FP*VN/8.314/TF
       IF(IREP.EQ.2)GOTO 86
       RFHO=1.0
44     WF=AWF*RFHO/(RFHO*AWF+(100.0-AWF))*100.0
       RFHOP=WF*(WF*A2+A1)+A0
       IF(DABS(RFHOP-RFHO).LT.0.00005) GOTO 43
       RFHO=RFHOP
       GOTO 44
```

```
43    CONTINUE
      GOTO 87
86    RFHO=1.0
34    WF=AWF*RFHO/(RFHO*AWF+(100.0-AWF))*100.0
      RFHOP=WF*(WF*A22+A12)+A02
      IF(DABS(RFHOP-RFHO).LT.0.00005) GOTO 33
      RFHO=RFHOP
      GOTO 34
33    CONTINUE
87    ZWF=WF*ZN/(100.-WF)
      GFT=ZN*28.01+ZWF*18.02+ZS1F*32.064
C
C       CALCULATION OF FEED COMPOSITION
C      ZT IS THE MOLE FLOW OF SULPHUR IF ALL S1
C      USED AS AN ESTIMATE TO FIND
C      THE EQUILIBRIUM COMPOSITION
C
      PRESS=RP/101325.
      T=TR
C
C     CALCULATIONS INCLUDING THE CALIBRATIONS
C
C     AREA %'S TO MOLE %'S
C
       IF(IREP.EQ.2) GOTO 88
       RFHO=1.0
45     DEN=RFHO*AWP+RFHS*AHSP+RFSD*ASDP+
C      1.0*(100.-AWP-AHSP-ASDP)
       WP=AWP*RFHO/DEN*100.0
       SDP=ASDP*RFSD/DEN*100.0
       HSP=AHSP*RFHS/DEN*100.0
       RFHOP=WP*(WP*A2+A1)+A0
       IF(DABS(RFHOP-RFHO).LT.0.00005) GOTO 46
       RFHO=RFHOP
       GOTO 45
46     CONTINUE
       GOTO 89
88     RFHO=1.0
35     DEN=RFHO*AWP+RFHS1*AHSP+RFSD1*ASDP+
C      1.0*(100.-AWP-AHSP-ASDP)
       WP=AWP*RFHO/DEN*100.0
       SDP=ASDP*RFSD1/DEN*100.0
       HSP=AHSP*RFHS1/DEN*100.0
       RFHOP=WP*(WP*A22+A12)+A02
       IF(DABS(RFHOP-RFHO).LT.0.00005) GOTO 89
       RFHO=RFHOP
       GOTO 35
89    CONTINUE
      ZWP=WP*ZN/(100-WP)
      ZHSP=HSP*ZN/(100-HSP)
      ZSDP=SDP*ZN/(100-SDP)
      ZWF=ZWP+ZHSP
      ZWF=WF*ZN/(100.-WF)
      GFT=ZN*28.01+ZWF*18.02+ZS1F*32.064
```

```
      ZFT=ZN+ZWF+ZS1F/8.0
C
C      CALCULATION OF REACTION EQUILIBRIUM CONSTANTS
C
      DO 20 J=1,7
      FRT(J)=FRE(J,1)*(1.-DLOG(T))-FRE(J,2)*
     #T/2.-FRE(J,3)*T*T/6.
     #-FRE(J,4)*(T**3)/12.-FRE(J,5)*(T**4)/20.
     #+FRE(J,6)/T-FRE(J,7)-FRE(J,8)/T/T
20    CONTINUE
      DFRT21=2.*FRT(1)+FRT(2)-1.5*FRT(4)-2.0*FRT(3)
      DFRT41=2.0*FRT(1)+FRT(2)-0.75*FRT(5)-2.*FRT(3)
      DFRT61=2.0*FRT(1)+FRT(2)-0.5*FRT(6)-2.*FRT(3)
      DFRT81=2.0*FRT(1)+FRT(2)-0.375*FRT(7)-2.*FRT(3)
      RK21=DEXP(-DFRT21)
      RK41=DEXP(-DFRT41)
      RK61=DEXP(-DFRT61)
      RK81=DEXP(-DFRT81)
      DFRT2=4.0*FRT(4)-FRT(7)
      DFRT4=2.0*FRT(5)-FRT(7)
      DFRT6=4.0/3.0*FRT(6)-FRT(7)
      RK2=DEXP(-DFRT2)
      RK4=DEXP(-DFRT4)
      RK6=DEXP(-DFRT6)
C
C           CALCULATION OF FEED COMPOSITION
C
C
C         ASSUMPTION THAT FEED IS S8, (FIRST APPROXIMATION)
C
      YHS=0.0
      YSO=0.0
      YW=ZWF/ZFT
      YS8=ZS1F/8.0/ZFT
      YN=ZN/ZFT
      W=1.0
      A=(PRESS**3*RK2)**0.25
      B=(PRESS*RK4)**0.5
      C=(PRESS**(1.0/3.0)*RK6)*0.75
      X(2)=1.0
      X(1)=YS8
      XIP=X(1)
      CONV=0.0
      DO 21    IW=1,50
      IF(IW.EQ.50) GOTO 32
      D=YN+YW+0.5*CONV*YW
      E=1.5*CONV*YW-8.0*YS8
      CALL NLSYST(X,A,B,C,D,E,F,W)
      FMF(8)=X(1)
      FMF(5)=(RK2*(PRESS/X(2))**3*X(1))**0.25
      FMF(6)=(RK4*PRESS/X(2)*X(1))**0.5
      FMF(7)=(RK6*(PRESS/X(2))**(1.0/3.0)*X(1))**0.75
      TFMF=YN+YW+FMF(5)+FMF(6)+FMF(7)+FMF(8)
16    FMF(1)=YN
```

```
      FMF(2)=YW
      FMF(3)=0.0
      FMF(4)=0.0
      GFT=0.0
      DO 17    I=1,8
      FPP(I)=FMF(I)*PRESS*101325.
      GF(I)=FMF(I)*WMOL(I)*ZFT
      GFT=GFT+GF(I)
   17 CONTINUE
      SGF=0.0
      DO 18    I=5,8
   18 SGF=SGF+GF(I)
      SGFA=ZS1F*32.064
      IF(DABS(SGFA-SGF).LT.0.1D-08) GOTO 19
      DS=SGFA/SGF
      X(1)=XIP*DS
      YS8=X(1)
      XIP=X(1)
      GOTO 21
   19 ZFT=ZFT*TFMF
      YN=ZN/ZFT
      YW=ZWF/ZFT
      YS8=FMF(8)
      X(1)=XIP
      X(2)=1.0
      IF(DABS(TFMF-1.000).LT.0.1D-08) GOTO 22
   21 CONTINUE
   22 VFT=ZFT*RT/RP
C
C       CALCULATION OF REACTOR CONVERSION
C
      CONV=(ZWF-ZWP)/ZWF
      X(2)=1.00
      XIP=X(1)
      XW=CONV
      ZPT=ZN+ZWP+(1.0-0.1875*XW)*ZS1F/8.0
      YN=ZN/ZPT
      YW=ZWP/ZN
      EMF(3)=ZHSP/ZPT
      EMF(4)=ZSDP/ZPT
      YS8=(1.0-0.1875*XW)*ZS1F/8.0/ZPT
      DO 25    IW=1,50
      IF(IW.EQ.50) GOTO 32
      D=YN+YW+0.5*CONV*YW
      E=1.5*CONV*YW-8.0*YS8
      CALL NLSYST(X,A,B,C,D,E,F,W)
      EMF(8)=X(1)
      EMF(5)=(RK2*(PRESS/X(2))**3*X(1))**0.25
      EMF(6)=(RK4*PRESS/X(2)*X(1))**0.5
      EMF(7)=(RK6*(PRESS/X(2))**(1.0/3.0)*X(1))**0.75
      EMF(1)=YN
      EMF(2)=YW
      TEMF=YN+YW+EMF(3)+EMF(4)+EMF(5)+EMF(6)+EMF(7)+EMF(8)
      GPT=0.0
```

```
      DO 23   I=1,8
      EPP(I)=EMF(I)*PRESS*101325.
      GP(I)=EMF(I)*WMOL(I)*ZPT
      GPT=GPT+GP(I)
23    CONTINUE
      SGP=(EMF(3)+EMF(4)+2.0*EMF(5)+4.0*EMF(6)+6.0*EMF(7)+
     &8.0*EMF(8))*32.064*ZPT
      IF(DABS(SGFA-SGP).LT.0.1D-08) GOTO 24
      DS=SGFA/SGP
      X(1)=XIP*DS
      YS8=X(1)
      XIP=X(1)
      GOTO 25
24    ZPT=ZPT*TEMF
      YN=ZN/ZPT
      YW=ZWP/ZPT
      EMF(3)=ZHSP/ZPT
      EMF(4)=ZSDP/ZPT
      YS8=EMF(8)
      X(1)=XIP
      X(2)=1.0
      IF(DABS(TEMF-1.000).LT.0.1D-08) GOTO 26
25    CONTINUE
C
C     ATOM BALANCES
C
26    AHF=FMF(2)*ZFT*2.0
      AOF=FMF(2)*ZFT
      ASF=ZS1F
      ATF=AHF+AOF+ASF
      AHP=(EMF(3)*2.0+EMF(2)*2.0)*ZPT
      AOP=(EMF(4)*2.0+EMF(2))*ZPT
      ASP=(EMF(3)+EMF(4)+2.0*EMF(5)+4.0*EMF(6)+
     & 6.0*EMF(7)+8.0*EMF(8))*ZPT
      ATP=AHP+AOP+ASP
      VFT=ZFT*RT/RP/60.0
      VPT=ZPT*RT/RP/60.0
      GFT=GFT/60.0
      GPT=GPT/60.0
      AHD=(AHP-AHF)/AHF*100.0
      AOD=(AOP-AOF)/AOP*100.0
      ASD=(ASP-ASF)/ASP*100.0
C
C     KINETIC CALCULATIONS
C
      TAU=0.001*VR/VPT/1000.
      SV=1.0/TAU
      XW=(ZWF-ZWP)/ZWF
      XS8=(FMF(8)*ZFT-EMF(8)*ZPT)/(FMF(8)*ZFT)
      XS6=(FMF(7)*ZFT-EMF(7)*ZPT)/(FMF(7)*ZFT)
      XS4=(FMF(6)*ZFT-EMF(6)*ZPT)/(FMF(6)*ZFT)
      XS2=(FMF(5)*ZFT-EMF(5)*ZPT)/(FMF(5)*ZFT)
      RATEW=(ZWF-ZWP)/WT/60.0
      RATES8=(FMF(8)*ZFT-EMF(8)*ZPT)/WT/60.0
```

```
      RATES6=(FMF(7)*ZFT-EMF(7)*ZPT)/WT/70.0
      RATES4=(FMF(6)*ZFT-EMF(6)*ZPT)/WT/60.0
      RATES2=(FMF(5)*ZFT-EMF(5)*ZPT)/WT/50.0
      RATEWS=RATES8*16.0/3.0
     **+RATES6*4.0+RATES4*8.0/3.0+RATES2*4.0/3.0
      RATED=(RATEW-RATEWS)/RATEW * 100.0
      WFS8=WT/(FMF(8)*ZFT*60.0)
      WFS6=WT/(FMF(7)*ZFT*60.0)
      WFS4=WT/(FMF(6)*ZFT*60.0)
      WFS2=WT/(FMF(5)*ZFT*60.0)
      WFW=WT/(60.0*ZWF)
C
C     OUTPUT
C
C
C     FULL CALCULATED VARIABLES
C
      DO 31  J=1,NREP
      WRITE(6,90) (RUNDAT(I),I=1,6),(RUNDAT(I),I=7,15)
90    FORMAT(1H1,////////,19X,'RUN ',6A1,15X,'DATE ',9A1)
      WRITE(6,91) WT
91    FORMAT(/,19X,'CATALYST  KA S201 ',4X,F10.4,' G')
      WRITE(6,92) PRESS,T,RPM
92    FORMAT(/,19X,'PRESSURE (ATM) ',F12.5,10X,
     1'TEMPERATURE (K) ',F12.2,10X,'FAN SPEED = ',F6.0,' RPM')
      WRITE(6,27 ) RATEW,RATES8,
     *RATES6,RATES4,RATES2,RATEWS,RATED
27    FORMAT(/,42X,'WATER',10X,'S8',12X,'S6',12X,'S4',
     &12X,'S2',
     &/,19X,'RATE (MOL/S G CAT)',5(2X,E12.5),/,19X,
     &'RATE (WS) = ',E12.5,
     &' MOL/S.GM CAT',5X,'% DIFFERENCE = ',F8.2)
      WRITE(6,94) TAU,SV,ZFT,ZPT,GFT,GPT,VFT,VPT
94    FORMAT(/,19X,'RESIDENCE TIME =  ',F8.2
     5,' S',/,19X,'SPACE VELOCITY = ',E12.4,' (1/S)',//,
     119X,'MOLE FLOW FEED = ',E12.4,5X,'PRODUCT ',E12.4,
     &' MOL/S',/,19X,'MASS FLOW ',
     2'FEED = ',E12.4,5X,'PRODUCT ',E12.4,' G/S',/,
     319X,'VOL  FLOW FEED = ',E12.4,5X,'PRODUCT ',E12.4,
     4' M3/S',/)
      WRITE(6,97)
97   FORMAT(46X,'FEED',40X,'REACTOR',//,19X,'SPECIES',1X,
     &'MOLE FRACTION',
     22X,'PARTIAL PRESS',3X,'MASS FLOW',
     37X,'MOLE FRACTION',1X,'PARTIAL PRESS',2X,
     4'MASS FLOW',/,46X,'(PASCAL)',7X,'(G/S)',24X,'(PASCAL)',
     58X,'(G/S)',/)
      DO 95 I=1,8
      GF(I)=GF(I)/60.0
      GP(I)=GP(I)/60.0
      WRITE(6,96) CHEM(I),FMF(I),FPP(I),GF(I),EMF(I),EPP(I)
     1,GP(I)
95    CONTINUE
96    FORMAT(19X,A4,3X,E12.5,4X,E12.5,4X,E12.5,
```

```
     14X,E12.5,2X,E12.5,3X,E12.5)
        WRITE(6,98) XW,XS8,XS6,XS4,XS2
98   FORMAT(/,39X,'WATER',11X,'S8',12X,'S6',12X,'S4',
     &12X,'S2',
     &/,19X,'CONVERSION        ',5(F8.4,6X))
        WRITE(6,99) WFW,WFS8,WFS6,WFS4,WFS2
99      FORMAT(19X,'WT CAT/MOL FEED ',5(2X,E12.5)/)
      WRITE(6,37)AHF,AHP,AHD,AOF,AOP,AOD,ASF,ASP,ASD
37   FORMAT(19X,'ATOM BALANCES   FEED',10X,' PRODUCT',5X,
     &'%DIFFERENCE',/,
     *19X,'HYDROGEN',E12.5,2X,E12.5,5X,F6.2,/,19X,'OXYGEN ',
     *E12.5,2X,E12.5,5X,F6.2,/,19X,'SULPHUR',E12.5,2X,E12.5,
     &5X,F6.2,/)
      WRITE(6,29 ) RK21,RK41,RK61,RK81
29   FORMAT(/,19X,'EQUILIBRIUM CONSTANTS',//,24X,'RK21=',
     &D13.6,5X,'RK41=',
     #D13.6,/,24X,'RK61=',D13.6,5X,'RK81=',D13.6)
      WRITE(6,30 ) RK2,RK4,RK6
30   FORMAT(/,24X,'RK2=',D13.6,3X,'RK4=',D13.6,3X,
C    'RK6=',D13.6,/)
      ICU=ICU+1
      IF(ICU.NE.5) GOTO 11
      IC=6
      IPAGE=1
      ICU=0
      GOTO 9
11     IC=0
      IPAGE=0
9     IF(RUNDAT(1).EQ.S) GOTO 82
      FA=WFW
      XA=XW
      GOTO 83
82    FA=WFS8
      XA=XS8
83    WRITE(11,71)IPAGE,IC
71    FORMAT(I1,/I1,9X,'RUN',4X,' DATE',6X,'PRESS',
     &3X,'TEMP',3X,'WT CAT',3X,'S.V.',8X,'WT/FA      CONV')
      WRITE(11,70)(RUNDAT(I),I=1,16),PRESS,T,WT,SV,FA,XA,
     *(FMF(I),I=1,8),(EMF(I),I=1,8)
70   FORMAT(10X,16A1,F8.4,F7.1,F9.4,E12.4,F8.2,3X,F8.5,
     &/,15X,'N2',10X,'WATER',7X,'H2S',9X,'SO2',11X,'S2',11X,
     &'S4',11X,'S6',11X,'S8',
     &/,10X,8E13.5,'    FEED',/,10X,8E13.5,'    PRODUCT',//)
      FMF(2)=FMF(2)*100.0
      FMF(8)=FMF(8)*100.0
      ITA=ITA+1
      IF(ITA.GT.1) GOTO 85
      WRITE(10,80) (RUNDAT(I),I=1,4)
80    FORMAT(1H1,20X,'DATA SET ',8A1,//)
      WRITE(10,81)
81    FORMAT(17X,'RUN',2X,'PRESSURE(ATM)',2X,
     &'TEMPERATURE(K)',2X,'WATER(%) FEED',2X,
     &'SULPHUR(%) FEED','   G.HR/MOL FEED',4X,'CONVERSION')
85    WRITE(10,84) (RUNDAT(I),I=1,5),PRESS,T,FMF(2),
```

```
     &FMF(8),
     &FA,XA
84     FORMAT(/,20X,5A1,F11.6,6X,F7.2,6X,
     &F10.6,9X,F10.6,6X,F13.6,F13.6)
31     CONTINUE
       IF(IREP.GT.0) GOTO 13
32     WRITE(6,36  )
36     FORMAT(///,20('*'),//,10X,'FEED CONCENTRATION NOT
     & CONVERGED',//,20('*'))
28     STOP
       END
C
C
C
C    SUBROUTINE NLSYST(X,A,B,C,D,E,F,W)
C THIS SUBROUTINE SOLVES A SYSTEM OF TWO NONLINEAR
C EQ'S BY NEWTONS'S METHOD.
C
       IMPLICIT REAL*8(A-H,O-Z,$)
       DIMENSION FSAVE(2),X(2),F(2,1),DF(2,2),
C      WKAREA(12),XSAVE(2)
38     FORMAT(5D14.5)
       M=1
       N=2
       IA=2
       IDGT=0
       MAXIT=50
       FTOL=.1D-09
       XTOL=.1D-08
       DO 48  I=1,MAXIT
       DO 10 J=1,2
10     XSAVE(J)=X(J)
       A4R=X(1)**0.25
       ZT4R=X(2)**0.25
       F(1,1)=E+2.0*A*A4R/(ZT4R**3)+4.0*B*A4R/(ZT4R*ZT4R)+
     &6.0*C*A4R**3/ZT4R+8.0*X(1)
       F(2,1)=A*A4R/(ZT4R**3)+B*A4R*A4R/(ZT4R*ZT4R)
     &+C*A4R**3/ZT4R +X(1)+D-X(2)
       ITEST=0
       DO 20 J=1,2
       IF(DABS(F(J,1)).GT.FTOL) ITEST=ITEST+1
       FSAVE(J)=F(J,1)
       F(J,1)=-F(J,1)
20     CONTINUE
       IF(ITEST.NE.0) GO TO 30
       RETURN
30     DF(1,1)=0.5*A/(A4R*ZT4R)**3+2.0*B/(A4R*ZT4R)**2+
     &4.5*C/(A4R*ZT4R)+8.0
       DF(1,2)=(-1.0/X(2))*(1.5*A*A4R/ZT4R**3+
     & 2.0*B*A4R*A4R/ZT4R**21.5*C*A4R**3/ZT4R)
       DF(2,1)=0.25*A/(ZT4R*A4R)**3+0.5*
     &B/(ZT4R*A4R)**2+0.75*C/(ZT4R*A4R)+1.0
       DF(2,2)=(-1.0/X(2))*(0.75*A*A4R/ZT4R**3+
     & 0.5*B*A4R*A4R/ZT4R**2+0.25*C*(A4R**3)/ZT4R)-1.0
```

```
      DF(1,2)=DF(1,2)/DF(1,1)
      F(1,1)=F(1,1)/DF(1,1)
      DF(1,1)=DF(1,1)/DF(1,1)
      DF(2,2)=DF(2,2)/DF(2,1)
      F(2,1)=F(2,1)/DF(2,1)
      DF(2,1)=DF(2,1)/DF(2,1)
      CALL LEQT1F(DF,M,N,IA,F,IDGT,WKAREA,IER)
39    X(1)=XSAVE(1)+W*F(1,1)
      X(2)=XSAVE(2)+W*F(2,1)
      W=W/2.0
      IF(X(1).LE.0.0) GOTO 39
      IF(X(2).GT.0.0) GOTO 47
      GOTO 39
47    ITEST=0
      W=1.0
      DO 50 JJ=1,2
      IF(DABS(F(JJ,1)).GT.XTOL) ITEST=ITEST+1
50    CONTINUE
C
C IF XTOL MET PRINT THE RESULT
C
      IF(ITEST.EQ.0) GO TO 49
48    CONTINUE
      RETURN
49    RETURN
      END
```

Operation of IRANAL and NLREG

Having obtained conversion versus mole flow rate data it remains to fit the data with a suitable function to obtain the initial rate from the slope at the origin. This slope may be obtained in several ways. A smooth curve can be drawn through the plot and the slope estimated by eye. A spline curve can be fitted to the data. A non-linear function can be fitted. This latter approach was used since it was consistent and also made use of all the data. The eye-fit would not be consistent, and the spline curve places a great deal of emphasis on the point closest the origin. All these methods were applied to the data, and the nonlinear curve fitting technique proved the most reliable. However, each method gave similar results, indicating that the use of each technique was valid.

The curve, A = tanh(B x), was used to fit the experimental data. This curve has the advantage that at the origin the slope is equal to A*B, the two parameters which are estimated by the least squares technique.

$$y = A \tanh(B x)$$

$$dy/dx = A \operatorname{sech}^2(B x)\, B$$

Hence at y = x = 0, dy/dx = A B, since, $\operatorname{sech}^2(0) = 1.0$

The least squares estimates of the parameters was obtained using the modified damped least squares (MDLS) non-linear curve fitting technique developed by Meyer and Roth (58). This method is illustrated by Wolfe (87).

The program IRANAL listed below, reads the experimental data and calls the subroutine NLREG, which returns with the values of the parameters A and B, as estimated using the MDLS method. A flow chart of this method can be found in the references cited above. This program requires two subroutines MODEL and MDER. MODEL calculates the value of the curve being fitted to the data.

MDER evaluates the derivatives with respect to the parameters, viz.

$$y = A \tanh(B\,x)$$

$$dy/dA = \tanh(B\,x)$$

$$dy/dB = A\,\mathrm{sech}^2(B\,x)\,x$$

The MDLS algorithm is based on the Gauss–Newton procedure. It is reported by its authors to be a reliable and efficient method of solving a general non–linear least squares problem. In this work, the method proved to be fast and reliable. The fitting on the Tanh curves had no difficulties. The fitting of the water function was slightly more difficult since the variables required scaling in order that a solution could be obtained. This scaling of the data has been described in Appendix 2.

The program ADSREG is included for completeness, although it is basically the same as IRANAL. The difference lies in the form of the function that is of interest and of course its derivatives.

```
      C
C #================================================#
C #                                                #
C #                    IRANAL                      #
C #                                                #
C #            Initial Rate analysis               #
C #                                                #
C #================================================#
C
C-----------------------------------------
C
C
C  MAINLINE PROGRAM FOR NON-LINEAR CURVE FITTING
C            OF:
C                  Y = A*TANH(B.X)
C
C           FOR INITIAL RATE DATA ANALYSIS
C-----------------------------------------------
C
        REAL LAMBDA
        DIMENSION DAT(5)
        DOUBLE PRECISION X(2),Y(15),T(15,1),W(15)
        DATA FSTAT,TSTAT,EXPVAR /1.5,2.5,0.0/
12      READ(4,80) ID
80      FORMAT(I2)
        IF(ID.LT.0) STOP
        READ(4,50) (DAT(I),I=1,5)
50      FORMAT(5A1)
        READ(4,40) TEMP,ET,ATM,EAT
40      FORMAT(F6.1,F5.2,2F12.8)
        READ(4,60) SXP,ESXP,WP,EWP
60      FORMAT(4F12.5)
        READ(4,10) N,M,L,LAMBDA,GAMMA
10      FORMAT(3I2,F5.2,E10.2)
        READ(4,20) X(1),X(2)
20      FORMAT(2F5.2)
        READ(4,13) SY,SX
13      FORMAT(2E12.5)
        DO 11 I=1,M
        READ(4,30) Y(I),T(I,1),W(I)
        Y(I)=SY*Y(I)
        T(I,1)=SX*T(I,1)
11      CONTINUE
30      FORMAT(3F12.5)
        WRITE(5,70) (DAT(I),I=1,4),TEMP,ET,
     & ATM,EAT,SXP,ESXP,WP,EWP,
70      FORMAT(//,'DATA SET ',4A1,//,
     &'TEMPERATURE = ',F6.1,' K   # ',
     &F4.1,/,'PRESSURE    =  ',F7.4,
     &' ATM   # ',F7.4,//,'SULPHUR ',
     &F12.5,' %  # ',F12.5,/,'WATER   ',
     &F12.5,' %  # ',F12.5,//,
     &5X,'SCALING FACTORS',/,2X,
     &'CONVERSION  *  ',E12.5,/,
```

```
     &2X,'PARTIAL PRESSURE * ',E12.5,//)
       CALL NLREG(N,M,L,X,Y,T,W,LAMBDA,
     &GAMMA,FSTAT,TSTAT,EXPVAR)
       IF(ID.GT.0) GOTO 12
       STOP
       END
C
CC_____________________________________________________________
C
C                  EVALUATION OF THE FUNCTION
C
       SUBROUTINE MODEL(N1,M1,N,M,L,X,T,I,VALUE)
       DOUBLEPRECISION X(N1),T(M,L)
       VALUE=X(1)*(DEXP(2.0*X(2)*T(I,1))-1.0)/
     #(DEXP(2.0*X(2)*T(I,1))+1.0)
       RETURN
       END
C
CC_____________________________________________________________
C
C      EVALUATION OF THE DERIVATIVES WRT THE PARAMETERS
C
       SUBROUTINE MDER(N1,M1,N,M,L,X,T,I,D)
       DOUBLE PRECISION X(N1),D(N1),T(M,L)
       D(1)=(DEXP(2.0*X(2)*T(I,1))-1.0)/
     #(DEXP(2.0*X(2)*T(I,1))+1.0)
       DUMI=2.0/(DEXP(X(2)*T(I,1))+
     #DEXP(-1.0*X(2)*T(I,1)))
       D(2)=X(1)*T(I,1)*DUMI*DUMI
       RETURN
       END
```

```
      C
C #================================================#
C #                                                #
C #                   ADSREG                       #
C #                                                #
C #          Initial Rate analysis                 #
C #                                                #
C #================================================#
C
C------------------------------------------------
C
C MAINLINE PROGRAM FOR NON-LINEAR CURVE FITTING
C OF:
C       Y = C*W**N/(1+K*W)**2.0
C
C       FOR INITIAL RATE DATA ANALYSIS
C------------------------------------------------
C
C      ID NEGATIVE IMPLIES NO MORE DATA
C         FOR ANALYSIS
C      THE NEXT THREE INPUT LINES ARE THE
C         SPECIFICATIONS OF THE DATA SET
C      N - NUMBER OF DATA POINTS
C      M - THE NUMBER OF PARAMETERS BEING ESTIMATED
C      L - THE NUMBER OF REPEAT DATA POINTS
C      ALAM AND GAMMA ARE VARIABLES GOVERNING THE
C          RATE OF APPROACH TO THE SOLUTION, SET
C          ALAM TO 0 AND GAMMA TO 10**(20) AS FIRST
C          GUESS.
C      X(I) ARE THE INITIAL GUESSES OF THE PARAMETERS
C      Y(I) ARE THE DEPENDENT VARIABLE VALUES
C      T(I,L) ARE THE INDEPENDENT VARIABLE VALUES
C      W(I) ARE THE WEIGHTING FACTORS FOR EACH
C          DATA POINT, NORMALLY EQUAL TO 1
C
C    **************************************************
C
      DIMENSION DAT(5)
      DOUBLE PRECISION X(3),Y(15),T(15,1),W(15)
      DATA FSTAT,TSTAT,EXPVAR /1.5,2.5,0.0/
12    READ(4,80) ID
80    FORMAT(I2)
      IF(ID.LT.0) STOP
      READ(4,50) (DAT(I),I=1,5)
50    FORMAT(5A1)
      READ(4,40) TEMP,ET,ATM,EAT
40    FORMAT(F6.1,F6.3,2F7.4)
      READ(4,60) SXP,ESXP,WP,EWP
60    FORMAT(4F12.5)
      READ(4,10) N,M,L,ALAM,GAMMA
10    FORMAT(3I2,F5.2,E10.2)
      READ(4,20) X(1),X(2),X(3)
20    FORMAT(3F5.2)
      DO 11 I=1,M
```

```
11   READ(4,30) Y(I),T(I,1),W(I)
30   FORMAT(3F12.9)
     WRITE(5,70) (DAT(I),I=1,5),TEMP,ET,ATM,EAT,
    &SXP,ESXP,WP,EWP
70   FORMAT(//,'DATA SET ',5A1,//,'TEMPERATURE = ',F6.1,
    * ' K   #',
    &F6.3,/,'PRESSURE    =  ',F7.4,' ATM   # ',F7.4,//,
    &'SULPHUR ',
    &F12.5,' %  # ',F12.5,/,'WATER   ',F12.5,' %  # ',
    &F12.5,//)
     WRITE(5,90)
90   FORMAT(//,10X,'Y = C*W**N/((1+K*W)**2.0)',//)
     CALL NLREG(N,M,L,X,Y,T,W,ALAM,GAMMA,FSTAT,TSTAT,EXPVAR)
     IF(ID.GT.0) GOTO 12
     STOP
     END
C
C    EVALUATION OF THE FUNCTION
C
     SUBROUTINE MODEL(N1,M1,N,M,L,X,T,I,VALUE)
     DOUBLEPRECISION X(N1),T(M,L)
     VALUE=(X(1)*T(I,1)**X(2))/((1.0+X(3)*T(I,1))**2.0)
     RETURN
     END
C
C   EVALUATION OF THE DERIVATIVES WRT THE PARAMETERS
C
     SUBROUTINE MDER(N1,M1,N,M,L,X,T,I,D)
     DOUBLE PRECISION X(N1),D(N1),T(M,L)
     D(1)=T(I,1)**X(2)/((1.0+X(3)*T(I,1))**2.0)
     DUMI=X(1)*T(I,1)**X(2)
     D(2)=DUMI*DLOG(T(I,1))/((1.0+X(3)*T(I,1))**2.0)
     D(3)=DUMI*(-2.0)*T(I,1)/((1.0+X(3)*T(I,1))**3.0)
     RETURN
     END
```

```
      C
C     **********************************
C     *                                *
C     *          NLREG                 *
C     *                                *
C     *    non-linear regression       *
C     **********************************
C
C-------------------------------------------------------
C
C  SUBPROGRAM FOR NONLINEAR LEAST-SQUARES REGRESSION
C
C  METHOD OF MEYER AND ROTH PRESENTED IN SECTION 7.7 OF
C
C    WOLFE,M.A.,'NUMERICAL METHODS FOR UNCONSTRAINED
C           OPTIMIZATION',VAN NOSTRAND REINHOLD,(1978).
C
C    R.B.NEWELL                    JULY,1979
C
C-------------------------------------------------------
C
      SUBROUTINE NLREG (N,M,L,X,Y,T,W,ALAM,GAMMA,
     *FSTAT,TSTAT,EXPVAR)
      INTEGER GTEST,ITEMP(10),JTEMP(10)
      DOUBLE PRECISION X(N),Y(M),T(M,L),W(M)
     *,XTIL(10),F(25),FTIL(25),G(10),A(25,10),XSVE(10)
     *,Q(10,10),P(10),TEMPN(10),TEMPNN(10,10)
     *,ALAM,GAMMA,FSTAT,TSTAT,EXPVAR
     *,BETA,EPS0,EPS1,EPS2,EPS3
     *,S,STIL,GTP,GMAX,TT,TP,DABS,DSQRT
      DATA N1,M1 / 10,25 /
      DATA BETA,EPS0,EPS1,EPS2,EPS3 / 1.D-05,.5D-06,.5D-06,
     C.5D-06,1.D-04 /
      LT=6
      WRITE (LT,890) LT
  890 FORMAT (' TERMINAL',I3,' - ENTER LUN FOR FULL OUTPUT')
      LU=7
      DO 13 IK=1,N
   13 XSVE(IK)=X(IK)
      NF=0
      ITER=0
C
C  INITIAL VALUES OF F AND S
C
      I=1
 8000 CONTINUE
      XTIL(I)=X(I)
      I=I+1
      IF(I.GT.N)GO TO  8001
      GO TO  8000
 8001 CONTINUE
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
C
C     START OF A MAIN ITERATION
```

```
C
 10   ITER=ITER+1
      IF (LU.GT.0) WRITE (LU,900) ITER
      IF (LT.NE.LU) WRITE (LT,900) ITER
 900  FORMAT (' ****************** MAIN ITERATION',I5)
      S=STIL
      I=1
 8002 CONTINUE
      X(I)=XTIL(I)
      I=I+1
      IF(I.GT.N)GO TO  8003
      GO TO  8002
 8003 CONTINUE
      I=1
 8004 CONTINUE
      F(I)=FTIL(I)
      I=I+1
      IF(I.GT.M)GO TO  8005
      GO TO  8004
 8005 CONTINUE
      IF (LU.GT.0) WRITE (LU,902) (X(I),I=1,N)
      IF (LT.NE.LU) WRITE (LT,902) (X(I),I=1,N)
 902  FORMAT (5D15.5)
      IF (LU.GT.0) WRITE (LU,904) S
      IF (LT.NE.LU) WRITE (LT,904) S
 904  FORMAT (' SUM-OF-SQUARES IS',D20.5)
C
C     SET UP THE LINEAR EQUATIONS
C
      IF (LU.GT.0) WRITE (LU,906) ALAM
 906  FORMAT (' ALAM IS',D15.4)
      CALL AX (N1,M1,N,M,L,XTIL,T,A,TEMPN)
      I=1
 8006 CONTINUE
      G(I)=0.D0
      K=1
 8008 CONTINUE
      G(I)=G(I)+A(K,I)*F(K)*W(K)
      K=K+1
      IF(K.GT.M)GO TO  8009
      GO TO  8008
 8009 CONTINUE
      TEMPN(I)=-G(I)
      I=I+1
      IF(I.GT.N)GO TO  8007
      GO TO  8006
 8007 CONTINUE
      I=1
 8010 CONTINUE
      J=1
 8012 CONTINUE
      Q(I,J)=0.D0
      K=1
 8014 CONTINUE
```

```
      Q(I,J)=Q(I,J)+A(K,I)*A(K,J)*W(K)
      K=K+1
      IF(K.GT.M)GO TO  8015
      GO TO  8014
 8015 CONTINUE
      IF (I.EQ.J) Q(I,J)=Q(I,J)*(1.D0+ALAM)
      J=J+1
      IF(J.GT.N)GO TO  8013
      GO TO  8012
 8013 CONTINUE
      I=I+1
      IF(I.GT.N)GO TO  8011
      GO TO  8010
 8011 CONTINUE
C
C     TRY TO SOLVE LINEAR EQUATIONS
C
      CALL SOLV (N1,M1,N,Q,P,TEMPN,TEMPNN,ITEMP,JTEMP,
     &EPS0,ISING)
      IF(ISING.EQ.0)GO TO  8016
      GO TO  8017
 8016 CONTINUE
C
C     CALCULATE (G)T.(P)
C
      GTP=0.D0
      I=1
 8019 CONTINUE
      GTP=GTP+G(I)*P(I)
      I=I+1
      IF(I.GT.N)GO TO  8020
      GO TO  8019
 8020 CONTINUE
C
C  AND CHECK THE SIZE OF (P)
C
      I=1
      GTEST=0
 8021 CONTINUE
      IF(DABS(P(I)).GT.GAMMA*DABS(X(I))) GO TO 8023
      GO TO  8024
 8023 CONTINUE
C
      GTEST=1
      WRITE (LT,910)
 910  FORMAT (/' ##### EXCESSIVELY LARGE GRADIENT #####'/)
      GO TO  8025
 8024 CONTINUE
 8025 CONTINUE
      I=I+1
      IF(I.GT.N.OR.GTEST.GT.0)GO TO  8022
      GO TO  8021
 8022 CONTINUE
      GO TO  8018
```

```
 8017 CONTINUE
 8018 CONTINUE
C
C  FIRST MAIN CHOICE ON SEARCH TYPE
C
      IF(ISING.EQ.1.OR.GTP.GE.0.D0.OR.GTEST.GT.0)GO TO  8026
      GO TO  8027
 8026 CONTINUE
C
C  DETERMINE GMAX
C
      GMAX=0.D0
      I=1
 8029 CONTINUE
      TT=DABS(G(I))
      IF(TT.GT.GMAX) GO TO  8031
      GO TO  8032
 8031 CONTINUE

      GMAX=TT
      LMAX=I
      GO TO  8033
 8032 CONTINUE
 8033 CONTINUE
      I=I+1
      IF(I.GT.N)GO TO  8030
      GO TO  8029
 8030 CONTINUE
C
C  SECOND MAIN CHOICE ON SEARCH TYPE
C
      IF(GMAX.LE.EPS1)GO TO  8034
      GO TO  8035
 8034 CONTINUE
C
C  PERFORM A GRID SEARCH
C
      IGRID=1
      CALL GRID (N1,M1,N,M,L,X,XTIL,Y,T,W,FTIL,STIL,NF,LU)
C
C  STOP IF NO SOS IMPROVEMENT
C
      ISTOP=1
      IF (STIL.GE.S) GO TO 90
C
C  OR GO ON TO ANOTHER ITERATION
C
      GO TO  8036
 8035 CONTINUE
C
C  PERFORM A LINE SEARCH
C
      IGRID=0
      I=1
```

```
 8037 CONTINUE
      P(I)=0.D0
      I=I+1
      IF(I.GT.N)GO TO  8038
      GO TO  8037
 8038 CONTINUE
      P(LMAX)=-G(LMAX)
      CALL LINE (N1,M1,N,M,L,X,P,S,XTIL,FTIL,STIL,Y,T,
     &W,NF,LU)
      ALAM=4.D0*ALAM
 8036 CONTINUE
      GO TO  8028
 8027 CONTINUE
C
C  PERFORM A BISECTION SEARCH
C
      IGRID=0
      CALL BISCT (N1,M1,N,M,L,X,P,S,XTIL,FTIL,STIL,
     *Y,T,W,BETA,GTP,NF,LU)
      ALAM=ALAM/4.D0
 8028 CONTINUE
C
C  IF A GRID SEARCH WAS DONE
C
      IF(IGRID.EQ.1)GO TO  8039
      GO TO  8040
 8039 CONTINUE
C
C  SKIP THE CONVERGENCE TESTING
C
      GO TO  8041
 8040 CONTINUE
C
C  CHECK CONVERGENCE
C
      TP=0.D0
      I=1
 8042 CONTINUE
      TP=TP+(XTIL(I)-X(I))*(XTIL(I)-X(I))
      I=I+1
      IF(I.GT.N)GO TO  8043
      GO TO  8042
 8043 CONTINUE
      IF(DSQRT(TP).LE.EPS2)GO TO  8044
      GO TO  8045
 8044 CONTINUE
C
      ICONV=1
      GO TO  8046
 8045 CONTINUE
      IF(DABS(STIL-S).LE.EPS3*S) GO TO  8047
      GO TO  8048
 8047 CONTINUE
```

```
      ICONV=2
      GO TO  8049
 8048 CONTINUE
      ICONV=0
 8049 CONTINUE
 8046 CONTINUE
C
C  TRY A GRID SEARCH IF CONVERGENCE INDICATED
C
      IF(ICONV.GT.0)GO TO  8050
      GO TO  8051
 8050 CONTINUE
C
      I=1
 8053 CONTINUE
      X(I)=XTIL(I)
      I=I+1
      IF(I.GT.N)GO TO  8054
      GO TO  8053
 8054 CONTINUE
      CALL GRID (N1,M1,N,M,L,X,XTIL,Y,T,W,FTIL,STIL,NF,LU)
      ISTOP=2
C
C  STOP IF NO SOS IMPROVEMENT
C
      IF (STIL.GE.S) GO TO 90
C
C  OR GO ON TO ANOTHER ITERATION
C
      GO TO  8052
 8051 CONTINUE
 8052 CONTINUE
 8041 CONTINUE
C
C  DO ANOTHER ITERATION IF WITHIN LIMIT
C
      ISTOP=3
      IF (ITER.LT.200) GO TO 10
C
C  STOP PROGRAM WITH APPROPRIATE PRINTOUT
C
 90   IF (LU.GT.0) WRITE (LU,950) ITER
      IF (LT.NE.LU) WRITE (LT,950) ITER
 950  FORMAT (' ########## OPTIMIZATION HALTED AFTER',
     C  I5,' ITERATIONS')
 8056 IF (ISTOP.EQ.1) GO TO  8057
      GO TO  8058
 8057 CONTINUE
      IF (LU.GT.0) WRITE (LU,952)
      IF (LT.NE.LU) WRITE (LT,952)
 952  FORMAT (' NO SOS IMPROVEMENT AFTER ILL-CONDITIONED',
     C  ' GRID SEARCH')
      GO TO  8105
 8058 IF (ISTOP.EQ.2) GO TO  8059
```

```
      GO TO  8060
 8059 CONTINUE
      IF (LU.GT.0) WRITE (LU,954) ICONV
      IF (LT.NE.LU) WRITE (LT,954) ICONV
 954  FORMAT (' NO SOS IMPROVEMENT FROM A GRID SEARCH',
     C  ' AFTER CONVERGENCE CHECK',I3)
      GO TO  8105
 8060 CONTINUE
      IF (LU.GT.0) WRITE (LU,956)
      IF (LT.NE.LU) WRITE (LT,956)
 956  FORMAT (' MAXIMUM ITERATIONS EXCEEDED WITHOUT ',
     C  'CONVERGENCE')
 8105 CONTINUE
      NC=M*NF+M*N*ITER
      IF (LU.GT.0) WRITE (LU,958) NC
      IF (LT.NE.LU) WRITE (LT,958) NC
 958  FORMAT (' EFFECTIVENESS MEASURE IS ',I10)
      WRITE (LT,960)
 960  FORMAT (' ENTER LUN FOR FULL PRINTOUT (0=NONE)')
       LU=5
      IF (LU.EQ.0) RETURN
      I=1
 8106 CONTINUE
      XTIL(I)=X(I)
      I=I+1
      IF(I.GT.N)GO TO  8107
      GO TO  8106
 8107 CONTINUE
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      CALL STATS (N1,M1,N,M,L,Y,T,W,XTIL,FTIL,STIL,A,Q,P,F,
     C  TEMPN,TEMPNN,ITEMP,JTEMP,EPSO,FSTAT,TSTAT,
     C  EXPVAR,LU,XSVE)
      RETURN
      END
C
C-------------------------------------------------------
C
C  EVALUATE F = Y(X,TDATA)-YDATA
C       AND S = (F)T.(F)
C
C-------------------------------------------------------
C
      SUBROUTINE FANDS (N1,M1,N,M,L,XTIL,Y,T,W,F,S,NF)
      DOUBLE PRECISION XTIL(N1),F(M1),Y(M),T(M,L),W(M)
     *,S,VALUE
      S=0.D0
      I=1
 8108 CONTINUE
      CALL MODEL (N1,M1,N,M,L,XTIL,T,I,VALUE)
      F(I)=VALUE-Y(I)
      S=S+F(I)*F(I)*W(I)
      I=I+1
      IF(I.GT.M)GO TO  8109
      GO TO  8108
```

```
 8109 CONTINUE
      NF=NF+1
      RETURN
      END
C
C-----------------------------------------------------
C
C  EVALUATE A(X) WHERE A(I,J)=DF(I)/DX(J)=DY(I)/DX(J)
C
C-----------------------------------------------------
C
      SUBROUTINE AX (N1,M1,N,M,L,XTIL,T,A,TEMPN)
      DOUBLE PRECISION T(M,L),XTIL(N1),A(M1,N1),TEMPN(N1)
      I=1
 8110 CONTINUE
      CALL MDER (N1,M1,N,M,L,XTIL,T,I,TEMPN)
      J=1
 8112 CONTINUE
      A(I,J)=TEMPN(J)
      J=J+1
      IF(J.GT.N)GO TO  8113
      GO TO  8112
 8113 CONTINUE
      I=I+1
      IF(I.GT.M)GO TO  8111
      GO TO  8110
 8111 CONTINUE
      RETURN
      END
C
C-------------------------------------------------
C
C  CALCULATE P IN THE RELATION (Q).(P) = (T)
C
C-------------------------------------------------
C
      SUBROUTINE SOLV (N1,M1,M,Q,P,T,TEMP,IROW,JROW,
     *EPS,ISING)
      DOUBLE PRECISION Q(N1,N1),P(N1),T(N1),TEMP(N1,N1)
     *,DSQRT,DABS,EL,AL,AMULT,EPS
      DIMENSION IROW(N1),JROW(N1)
      ISING=1
C
C  SET P TO T AND IROW TO ZERO
C
      I=1
 8114 CONTINUE
      P(I)=T(I)
      IROW(I)=0
      I=I+1
      IF(I.GT.M)GO TO  8115
      GO TO  8114
 8115 CONTINUE
C
```

```
C  COPY Q INTO TEMP
C
      J=1
 8116 CONTINUE
      I=1
 8118 CONTINUE
      TEMP(I,J)=Q(I,J)
      I=I+1
      IF(I.GT.M)GO TO  8119
      GO TO  8118
 8119 CONTINUE
      J=J+1
      IF(J.GT.M)GO TO  8117
      GO TO  8116
 8117 CONTINUE
C
C  FOR EACH OF THE M COLUMNS IN TEMP
C
      JJ=1
 8120 CONTINUE
C
C  FIND THE LARGEST ELEMENT IN THE COLUMN
C
      EL=-1.D35
      I=1
 8122 CONTINUE
      AL=DABS(TEMP(I,JJ))
      IF(IROW(I).EQ.0.AND.AL.GT.EL) GO TO  8124
      GO TO  8125
 8124 CONTINUE

      EL=AL
      IL=I
      GO TO  8126
 8125 CONTINUE
 8126 CONTINUE
      I=I+1
      IF(I.GT.M)GO TO  8123
      GO TO  8122
 8123 CONTINUE
C
C  CHECK ON MAGNITUDE FOR CONDITIONING
C
      IF (EL.LT.EPS) RETURN
C
C  SAVE ROW POSITION
C
      IROW(IL)=JJ
      JROW(JJ)=IL
C
C  FORWARD ELIMINATION PHASE
C
      I=1
 8127 CONTINUE
```

```
C
C  FOR EACH ROW NOT YET ELIMINATED
C
      IF(IROW(I).EQ.0)GO TO  8129
      GO TO  8130
 8129 CONTINUE
C
C  CALCULATE A MULTIPLIER
C
      AMULT=TEMP(I,JJ)/TEMP(IL,JJ)
      TEMP(I,JJ)=0.D0
C
C  ELIMINATION ON TEMP
C
      J=JJ+1
 8132 CONTINUE
      TEMP(I,J)=TEMP(I,J)-AMULT*TEMP(IL,J)
      J=J+1
      IF(J.GT.M)GO TO  8133
      GO TO  8132
 8133 CONTINUE
C
C  ELIMINATION ON P
C
      P(I)=P(I)-AMULT*P(IL)
      GO TO  8131
 8130 CONTINUE
 8131 CONTINUE
      I=I+1
      IF(I.GT.M)GO TO  8128
      GO TO  8127
 8128 CONTINUE
      JJ=JJ+1
      IF(JJ.GT.M) GO TO  8121
      GO TO  8120
 8121 CONTINUE
C
C  BACKWARD ELIMINATION FOR EACH COLUMN
C
      JJ=M
 8134 CONTINUE
      IL=JROW(JJ)
C
C  FOR EACH ROW DUE TO BE ELIMINATED
C
      I=1
 8136 CONTINUE
      IF(I.NE.IL.AND.TEMP(I,JJ).NE.0.D0) GO TO  8138
      GO TO  8139
 8138 CONTINUE
C
C  CALCULATE A MULTIPLIER
C
      AMULT=TEMP(I,JJ)/TEMP(IL,JJ)
```

```
      TEMP(I,JJ)=0.D0
C
C  ELIMINATE ON P
C
      P(I)=P(I)-AMULT*P(IL)
      GO TO  8140
 8139 CONTINUE
 8140 CONTINUE
      I=I+1
      IF(I.GT.M)GO TO  8137
      GO TO  8136
 8137 CONTINUE
      JJ=JJ-1
      IF(JJ.LT.1) GO TO  8135
      GO TO  8134
 8135 CONTINUE
C
C  NORMALIZATION PHASE
C
      I=1
 8141 CONTINUE
      IL=IROW(I)
      P(I)=P(I)/TEMP(I,IL)
      I=I+1
      IF(I.GT.M)GO TO  8142
      GO TO  8141
 8142 CONTINUE
C
C  REARRANGE ROWS
C
      J=1
 8143 CONTINUE
      IL=IROW(J)
      TEMP(IL,1)=P(J)
      J=J+1
      IF(J.GT.M)GO TO  8144
      GO TO  8143
 8144 CONTINUE
      J=1
 8145 CONTINUE
      P(J)=TEMP(J,1)
      J=J+1
      IF(J.GT.M)GO TO  8146
      GO TO  8145
 8146 CONTINUE
      ISING=0
      RETURN
      END
C
C-------------------------------------------------------------
C
C  PERFORM A GRID SEARCH OF S(X+GAMMA(J)*X(I)*E(I))
C    WHERE I = 1,2,....,N AND J = 1,..,4
C          E(I) = UNIT VECTOR
```

```
C          GAMMA = (0.1,-0.1,0.01,-0.01)T
C
C-------------------------------------------------------------
C
      SUBROUTINE GRID (N1,M1,N,M,L,X,XTIL,Y,T,W,FTIL,
     *STIL,NF,LU)
      DOUBLE PRECISION GAMMA(4),X(N),XTIL(N1),Y(M),T(M,L),
     *FTIL(M1),W(M),SMIN,STIL,S
      DATA GAMMA/.1D0,-.1D0,.01D0,-.01D0/
      IF(LU.GT.0) WRITE (LU,900)
 900  FORMAT (' GRID SEARCH: PRINTOUT OF STIL      XTIL')
      SMIN=1.D+35
      I=1
 8150 CONTINUE
      XTIL(I)=X(I)
      I=I+1
      IF(I.GT.N)GO TO  8151
      GO TO  8150
 8151 CONTINUE
      J=1
 8152 CONTINUE
      I=1
 8154 CONTINUE
C
C  CALCULATE A SEARCH POINT
C
      XTIL(I)=XTIL(I)*(1.D0+GAMMA(J))
      IF (I.GT.1) XTIL(I-1)=X(I-1)
C
C  EVALUATE THE SOS
C
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      IF (LU.GT.0) WRITE (LU,910) STIL,(XTIL(K),K=1,N)
 910  FORMAT (5D15.5)
C
C  CHECK IT
C
      IF(STIL.LT.SMIN)GO TO  8156
      GO TO  8157
 8156 CONTINUE
C
      SMIN=STIL
      JMIN=J
      IMIN=I
      GO TO  8158
 8157 CONTINUE
 8158 CONTINUE
      I=I+1
      IF(I.GT.N)GO TO  8155
      GO TO  8154
 8155 CONTINUE
      XTIL(N)=X(N)
      J=J+1
      IF(J.GT.4)GO TO  8153
```

```
      GO TO  8152
 8153 CONTINUE
C
C  SET UP THE MINIMUM POINT
C
      XTIL(IMIN)=XTIL(IMIN)*(1.D0+GAMMA(JMIN))
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      IF (LU.GT.0) WRITE (LU,920) STIL
 920  FORMAT (' MINIMUM STIL IN GRID IS',D15.5)
      IF (LU.GT.0) WRITE (LU,910) (XTIL(I),I=1,N)
      RETURN
      END
C
C-------------------------------------------------
C
C  PERFORM A LINEAR SEARCH
C
C-------------------------------------------------
C
      SUBROUTINE LINE (N1,M1,N,M,L,X,P,S,XTIL,FTIL,STIL,
     C   Y,T,W,NF,LU)
      DOUBLE PRECISION P(N1),X(N),XTIL(N1),FTIL(M1),Y(M),
     *,W(M),SE,STIL,S,PTP,H,TP,SBAR,ALPHA,DEL,DSQRT,DABS,
     *T(M,L)
      SE=0.D0
      STIL=S
C
C  CALCULATE (P)T.(P)
C
      PTP=0.D0
      I=1
 8159 CONTINUE
      PTP=PTP+P(I)*P(I)
      I=I+1
      IF(I.GT.N)GO TO  8160
      GO TO  8159
 8160 CONTINUE
C
C  CALCULATE H
C
      H=(S-SE)/PTP/2.D0
      TP=.5D0/DSQRT(PTP)
      IF (TP.LT.H) H=TP
C
C  FIRST SEARCH
C
 8161 CONTINUE
      SBAR=STIL
      H=2.D0*H
      I=1
 8163 CONTINUE
      XTIL(I)=X(I)+H*P(I)
      I=I+1
      IF(I.GT.N)GO TO  8164
```

```
      GO TO  8163
 8164 CONTINUE
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      IF (LU.GT.0) WRITE (LU,900) H,STIL
 900  FORMAT (' FIRST LINEAR SEARCH: H =',D15.5,
     C    '  SOS =',D15.5)
      IF (LU.GT.0) WRITE (LU,910) (XTIL(I),I=1,N)
 910  FORMAT (5D15.5)
      IF(STIL.GE.SBAR)GO TO  8162
      DO 100 IK=1,N
100   X(IK)=XTIL(IK)
      S=STIL
      GO TO  8161
 8162 CONTINUE
C
C  SECOND SEARCH
C
      ITR=1
 8165 CONTINUE
      ITR=ITR+1
      ALPHA=H*H*PTP/(STIL-S+2.D0*H*PTP)
      IF(ALPHA.GE.0.25D0*H.AND.ALPHA.LE.0.75D0*H) GOTO 8167
      GO TO  8168
 8167 CONTINUE

      DEL=ALPHA
      IDEL=0
      GO TO  8169
 8168 CONTINUE
      DEL=0.75D0*H
      IF (ALPHA.LT.DEL) DEL=ALPHA
      IF (H/4.D0.GT.DEL) DEL=H/4.D0
      IDEL=1
 8169 CONTINUE
      I=1
 8170 CONTINUE
      XTIL(I)=X(I)+DEL*P(I)
      I=I+1
      IF(I.GT.N)GO TO  8171
      GO TO  8170
 8171 CONTINUE
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      IF (LU.GT.0) WRITE (LU,920) DEL,STIL
 920  FORMAT (' SECOND LINEAR SEARCH: DEL =',D15.5,
     C    '  SOS =',D15.5)
      IF (LU.GT.0) WRITE (LU,910) (XTIL(I),I=1,N)
      IF(STIL.LT.S) GO TO  8172
      GO TO  8173
 8172 CONTINUE
      DO 110 IK=1,N
110   X(IK)=XTIL(IK)
      S=STIL

      ICONV=1
```

```
      GO TO  8174
 8173 CONTINUE
      ICONV=0
      IF (IDEL.EQ.0) H=DEL
 8174 CONTINUE
      IF(ICONV.EQ.1.OR.ITR.GT.15) GO TO  8166
      GO TO  8165
 8166 CONTINUE
      IF(ITR.LE.15) GO TO 8148
      DO 8147 I=1,N
 8147 XTIL(I)=X(I)
      S=STIL
 8148 CONTINUE
      RETURN
      END
C
C-------------------------------------------------------
C
C  PERFORM A BISECTION-TYPE SEARCH
C
C-------------------------------------------------------
C
      SUBROUTINE BISCT (N1,M1,N,M,L,X,P,S,XTIL,FTIL,STIL,
     C    Y,T,W,BETA,GTP,NF,LU)
      DOUBLE PRECISION X(N),P(N1),XTIL(N1),FTIL(M1),Y(M),
     *T(M,L),W(M),ALPHA,STIL,S,BETA,GTP
      IF (LU.GT.0) WRITE (LU,900) BETA,GTP
  900 FORMAT (' BISECTION SEARCH WITH BETA =',D15.5,
     C   ' AND GTP =',D15.5)
      ALPHA=2.D0
 8175 CONTINUE
      ALPHA=ALPHA/2.D0
      I=1
 8177 CONTINUE
      XTIL(I)=X(I)+ALPHA*P(I)
      I=I+1
      IF(I.GT.N)GO TO  8178
      GO TO  8177
 8178 CONTINUE
      CALL FANDS (N1,M1,N,M,L,XTIL,Y,T,W,FTIL,STIL,NF)
      IF (LU.GT.0) WRITE (LU,910) ALPHA,STIL
  910 FORMAT (' ALPHA =',D15.5,' SOS = ',D15.5)
      IF (LU.GT.0) WRITE (LU,920) (XTIL(I),I=1,N)
  920 FORMAT (5D15.5)
      IF(STIL.LE.(S+2.D0*BETA*ALPHA*GTP)) GO TO  8176
      GO TO  8175
 8176 CONTINUE
      RETURN
      END
C
C-------------------------------------------------------
C
C  FULL PRINTOUT AND STATISTICAL MEASURES
C
```

```
C-------------------------------------------------------
C
      SUBROUTINE STATS (N1,M1,N,M,L,Y,T,W,XTIL,FTIL,STIL,
     C   A,Q,P,F,TEMPN,TEMPNN,ITEMP,JTEMP,EPS0,
     C   FSTAT,TSTAT,EXPVAR,LU,XSVE)
      DOUBLE PRECISION Y(M),T(M,L),W(M),XTIL(N1),FTIL(M1),
     *A(M1,N1),
     *CQ(N1,N1),P(N1),TEMPN(N1),TEMPNN(N1,N1),F(M1),XSVE(N1)
     *,STIL,EPS0,FSTAT,TSTAT,EXPVAR,S1,S2,YBAR,PROP,VAR
     *,XU,XL,C,SBND,SAVEI,SAVEJ,XT,XP,VARY,DBLE,DSQRT,DABS
      DIMENSION ITEMP(N1),JTEMP(N1)
      WRITE (5,900) N
  900 FORMAT ('0',/,'                NONLINEAR REGRESSION'
     C ,' PROGRAM',//,' METHOD OF MEYER AND ROTH FROM'
     C ,' THE TEXT OF WOLFE,M.A.',/,'NUMERICAL'
     C ,' METHODS FOR UNCONSTRAINED OPTIMIZATION',
     C /,' VAN NOSTRAND REINHOLD, (1978).',//,' ESTIMATES'
     C ,' FOR THE',I3,' PARAMETERS ARE:',/)
      WRITE (5,910) (XTIL(I),I=1,N)
  910 FORMAT (6D12.4)
      WRITE(5,915)
  915 FORMAT(//,' THE INITIAL PARAMETER VALUES WERE:',/)
      WRITE(5,910) (XSVE(I),I=1,N)
      WRITE (5,920) STIL
  920 FORMAT (/' WEIGHTED SUM-OF-SQUARES IS',D12.4,////)
      DO 20 I=1,M
   20 FTIL(I)=FTIL(I)+Y(I)
      WRITE(5,930)
  930 FORMAT('PREDICTED Y','ACTUAL Y',
     *  'WEIGHTING','X VALUE')
      DO 25 IK=1,M
   25 WRITE(5,940) FTIL(IK),Y(IK),W(IK),T(IK,1)
  940 FORMAT(11D11.4)
      WRITE(5,950)
  950 FORMAT('1')
      RETURN
      END
```

APPENDIX 4 Results

This Appendix contains the full experimental results as given by the data analysis computer programs. The raw experimental data that was obtained has been summarised and only the feed and product mole fractions have been given. There are four sections, each of which is preceded by a description of that section.

1. The first section contains an example of the full output that was obtained from the program EXPTCAL and illustrates the kinetic and thermodynamic data that were calculated using this program.
2. The next section contains a summary of all the experimental data that were obtained throughout the course of this study.
3. The third section presents the output from the non-linear least squares program, NLSYST using the main program IRANAL. It contains the best fit estimate of the parameters of the Tanh curve, A and B, and hence the initial rates.
4. The final section contains the output from the non-linear least squares program using ADSREG as the main program. ADSREG is a main program similar to IRANAL but containing a different function. This function gives the best fit estimates of the parameters which model the water dependence of the reverse Claus reaction.

A listing of the computer programs that were used is given in Appendix 3.

Output from EXPTCAL, full experimental results from data set, W101A

1. Pressure and Temperature conditions are those inside the reactor.
2. RATE(WS) = total sulphur rate * stoichiometry.
3. The volumetric feed is calculated at the reactor conditions.
4. The feed partial pressures are those at the reactor conditions.
5. The following reactions have their equilibrium constants designated as follows.

$2\ H_2O + 3/8\ S_8 \rightleftharpoons SO_2 + 2\ H_2S$	RK81
$2\ H_2O + 3/6\ S_6 \rightleftharpoons SO_2 + 2\ H_2S$	RK61
$2\ H_2O + 3/4\ S_4 \rightleftharpoons SO_2 + 2\ H_2S$	RK41
$2\ H_2O + 3/2\ S_2 \rightleftharpoons SO_2 + 2\ H_2S$	RK21
$4\ S_2 \rightleftharpoons S_8$	RK2
$2\ S_4 \rightleftharpoons S_8$	RK4
$4/3\ S_6 \rightleftharpoons S_8$	RK6

RUN WIO1A DATE ,19/11/80

CATALYST KA S201 0.6079 G

PRESSURE (ATM) 1.47376 TEMPERATURE (K) 593.15 FAN SPEED = 1200. RPM

	WATER	S8	S6	S4	S2
RATE (MOL/S G CAT)	0.79331E-06	0.11085E-06	0.97335E-07	0.25763E-09	0.21710E-08

RATE (WS) = 0.98412E-06 MOL/S.GM CAT % DIFFERENCE = -24.05

RESIDENCE TIME = 64.65 S
SPACE VELOCITY = 0.1547E-01 (1/S)

MOLE FLOW FEED = 0.1864E-01 PRODUCT 0.1866E-01 MOL/S
MASS FLOW FEED = 0.9360E-02 PRODUCT 0.9364E-02 G/S
VOL FLOW FEED = 0.1026E-04 PRODUCT 0.1027E-04 M3/S

	FEED			REACTOR		
SPECIES	MOLE FRACTION	PARTIAL PRESS (PASCAL)	MASS FLOW (G/S)	MOLE FRACTION	PARTIAL PRESS (PASCAL)	MASS FLOW (G/S)
N2	0.97655E+00	0.14583E+06	0.84981E-02	0.97550E+00	0.14567E+06	0.84981E-02
H20	0.11436E-01	0.17078E+04	0.64026E-04	0.98734E-02	0.14744E+04	0.55335E-04
H2S	0.0	0.0	0.0	0.19345E-02	0.28887E+03	0.20504E-04
S02	0.0	0.0	0.0	0.11385E-02	0.17001E+03	0.22683E-04
S2	0.39918E-03	0.59609E+02	0.79532E-05	0.39521E-03	0.59016E+02	0.78827E-05
S4	0.24029E-04	0.35882E+01	0.95749E-06	0.23499E-04	0.35091E+01	0.93740E-06
S6	0.67450E-02	0.10072E+04	0.40314E-03	0.65158E-02	0.97299E+03	0.38986E-03
S8	0.48459E-02	0.72363E+03	0.38618E-03	0.46240E-02	0.69050E+03	0.36890E-03

	WATER	S8	S6	S4	S2
CONVERSION	0.1357	0.0448	0.0329	0.0210	0.0089
WT CAT/MOL FEED	0.47526E+02	0.11216E+03	0.80581E+02	0.22620E+05	0.13618E+04

ATOM BALANCES	FEED	PRODUCT	%DIFFERENCE
HYDROGEN	0.42636E-03	0.44069E-03	3.36
OXYGEN	0.21318E-03	0.22674E-03	5.98
SULPHUR	0.14937E-02	0.14937E-02	0.00

EQUILIBRIUM CONSTANTS

RK21= 0.905599E+01 RK41= 0.156964E+00
RK61= 0.594850E-03 RK81= 0.343291E-03

RK2= 0.162157E-11 RK4= 0.805937E-07 RK6= 0.230856E+00

Summary of All Experimental Data

Explanation of terms,

SI04A, sulphur initial rate data set, 0.4% total sulphur.

WI01A, water initial rate data set, 1% water in feed.

WT6HA, Temperature data set, 6% water, High temperature.

D0600, Diffusion test data set, impeller speed 600 rpm.

PRESS = pressure in atmospheres.

TEMP = temperature in Kelvin.

WT CAT = weight of catalyst, g.

S.V. = space velocity, 1/s.

WT/FA = inverse mole flow rate, g hr/mol.

CONV = conversion

The feed and reactor mol fractions of each component are given.

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04C,	24/07/80.	1.4684	601.1	10.0066	0.8264E-01	1147.94	0.21418			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97509E+00	0.19994E-01	0.0	0.0	0.39090E-03	0.17191E-04	0.30229E-02	0.14848E-02	FEED		
0.97348E+00	0.16890E-01	0.37854E-02	0.17772E-02	0.36900E-03	0.15257E-04	0.25224E-02	0.11649E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04B,	24/07/80.	1.4049	600.1	10.0066	0.6868E-01	1449.82	0.23158			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97426E+00	0.20938E-01	0.0	0.0	0.36479E-03	0.16236E-04	0.29450E-02	0.14761E-02	FEED		
0.97255E+00	0.17622E-01	0.40204E-02	0.19003E-02	0.34250E-03	0.14251E-04	0.24165E-02	0.11323E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04A,	24/07/80.	1.4049	601.1	10.0066	0.4333E-01	2307.21	0.24604			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97473E+00	0.20429E-01	0.0	0.0	0.37735E-03	0.16745E-04	0.29709E-02	0.14724E-02	FEED		
0.97331E+00	0.16484E-01	0.42976E-02	0.20289E-02	0.35269E-03	0.14562E-04	0.24039E-02	0.11085E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04D,	06/08/80.	1.4613	604.5	10.0066	0.3754E-01	2341.57	0.32423			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97631E+00	0.18259E-01	0.0	0.0	0.44726E-03	0.19969E-04	0.33427E-02	0.16212E-02	FEED		
0.97357E+00	0.13087E-01	0.63779E-02	0.29621E-02	0.40742E-03	0.16451E-04	0.24906E-02	0.10925E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04F,	10/08/80.	1.4639	601.3	9.0041	0.7643E-01	1017.40	0.22762			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97554E+00	0.19151E-01	0.0	0.0	0.40236E-03	0.18134E-04	0.32555E-02	0.16360E-02	FEED		
0.97355E+00	0.15685E-01	0.42060E-02	0.22266E-02	0.37836E-03	0.15959E-04	0.26813E-02	0.12611E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4G,	24/08/80.	1.4708	598.4	9.0041	0.3701E-01	2004.87	0.23402			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97369E+00	0.20975E-01	0.0	0.0	0.36873E-03	0.16873E-04	0.32503E-02	0.16985E-02	FEED	
	0.97167E+00	0.17285E-01	0.44217E-02	0.23022E-02	0.34606E-03	0.14788E-04	0.26604E-02	0.12983E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4I,	26/08/80.	1.4641	596.9	9.0041	0.7496E-01	978.43	0.22830			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97628E+00	0.18408E-01	0.0	0.0	0.34999E-03	0.16147E-04	0.32279E-02	0.17220E-02	FEED	
	0.97418E+00	0.14925E-01	0.42894E-02	0.22820E-02	0.32907E-03	0.14205E-04	0.26567E-02	0.13260E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4H,	26/08/80.	1.4612	595.5	9.0041	0.5891E-01	1239.32	0.21008			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97414E+00	0.20591E-01	0.0	0.0	0.33311E-03	0.15444E-04	0.31875E-02	0.17288E-02	FEED	
	0.97229E+00	0.17339E-01	0.39459E-02	0.20646E-02	0.31493E-03	0.13744E-04	0.26699E-02	0.13630E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4J,	11/09/80.	1.4673	595.5	5.0086	0.3695E-01	1088.68	0.21582			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97344E+00	0.21270E-01	0.0	0.0	0.33459E-03	0.15517E-04	0.32032E-02	0.17377E-02	FEED	
	0.97168E+00	0.17749E-01	0.42665E-02	0.19434E-02	0.31579E-03	0.13759E-04	0.26687E-02	0.13602E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4K,	11/09/80	1.4673	595.5	5.0086	0.5868E-01	690.01	0.19358			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97382E+00	0.20915E-01	0.0	0.0	0.33403E-03	0.15465E-04	0.31871E-02	0.17261E-02	FEED	
	0.97229E+00	0.17745E-01	0.38469E-02	0.16824E-02	0.31736E-03	0.13905E-04	0.27117E-02	0.13898E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4L,	12/09/80,	1.4643	596.9	5.0086	0.7442E-01	543.64	0.16835			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97550E+00	0.19150E-01	0.0	0.0	0.35068E-03	0.16209E-04	0.32461E-02	0.17348E-02	FEED		
0.97413E+00	0.16393E-01	0.33782E-02	0.14796E-02	0.33565E-03	0.14797E-04	0.28264E-02	0.14407E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4M,	06/08/80,	1.4613	602.6	10.0066	0.5944E-01	1460.40	0.29743			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97458E+00	0.20048E-01	0.0	0.0	0.42013E-03	0.18885E-04	0.32988E-02	0.16359E-02	FEED		
0.97214E+00	0.15263E-01	0.58208E-02	0.26977E-02	0.38625E-03	0.15860E-04	0.25308E-02	0.11465E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4P,	09/10/80,	1.4783	591.1	1.5975	0.7742E-01	167.53	0.09035			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97695E+00	0.18063E-01	0.0	0.0	0.28615E-03	0.13302E-04	0.29984E-02	0.16918E-02	FEED		
0.97620E+00	0.16721E-01	0.16864E-02	0.77164E-03	0.27977E-03	0.12693E-04	0.27925E-02	0.15378E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4O,	09/10/80,	1.4736	591.1	1.5975	0.5974E-01	213.75	0.10895			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97369E+00	0.21248E-01	0.0	0.0	0.28679E-03	0.13405E-04	0.30379E-02	0.17235E-02	FEED		
0.97330E+00	0.19066E-01	0.20637E-02	0.95608E-03	0.27901E-03	0.12663E-04	0.27867E-02	0.15351E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO4N,	09/10/80,	1.4783	591.1	1.5975	0.3667E-01	336.06	0.13434			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97328E+00	0.21514E-01	0.0	0.0	0.28987E-03	0.13650E-04	0.31168E-02	0.17814E-02	FEED		
0.97220E+00	0.19339E-01	0.26238E-02	0.12101E-02	0.28010E-03	0.12711E-04	0.27967E-02	0.15404E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04Q,	10/11/80,	1.4754	591.1	0.6079	0.3538E-01	126.99	0.08760			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97269E+00	0.21921E-01	0.0	0.0	0.29267E-03	0.13942E-04	0.32202E-02	0.18619E-02	FEED		
0.97224E+00	0.20166E-01	0.17254E-02	0.86659E-03	0.28637E-03	0.13325E-04	0.30065E-02	0.16980E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04R,	11/11/80,	1.4757	591.1	0.6079	0.5788E-01	80.91	0.05861			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97405E+00	0.20736E-01	0.0	0.0	0.28967E-03	0.13655E-04	0.31212E-02	0.17858E-02	FEED		
0.97352E+00	0.19846E-01	0.10784E-02	0.58876E-03	0.28554E-03	0.13253E-04	0.29826E-02	0.16803E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI04S,	11/11/80,	1.4781	591.1	0.6079	0.7152E-01	62.84	0.04630			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97413E+00	0.20490E-01	0.0	0.0	0.29290E-03	0.13939E-04	0.32162E-02	0.18577E-02	FEED		
0.97367E+00	0.19788E-01	0.85408E-03	0.50773E-03	0.28963E-03	0.13616E-04	0.31035E-02	0.17709E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05,	18/07/80,	1.3477	601.1	10.0066	0.3569E-01	2186.42	0.23501			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97114E+00	0.22822E-01	0.0	0.0	0.39335E-03	0.18961E-04	0.36547E-02	0.19677E-02	FEED		
0.96897E+00	0.18458E-01	0.52468E-02	0.24464E-02	0.36923E-03	0.16613E-04	0.29887E-02	0.15019E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05B,	20/07/80,	1.3484	603.1	10.0066	0.5092E-01	1379.61	0.20076			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96960E+00	0.23702E-01	0.0	0.0	0.43299E-03	0.21336E-04	0.40473E-02	0.21913E-02	FEED		
0.96772E+00	0.19402E-01	0.49655E-02	0.23104E-02	0.41082E-03	0.19106E-04	0.34206E-02	0.17479E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05C,	21/07/80,	1.3461	603.1	10.0066	0.6632E-01	1080.50	0.18594			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96925E+00		0.24157E-01	0.0		0.0	0.43046E-03	0.21124E-04	0.39908E-02	0.21519E-02	FEED
0.96740E+00		0.20378E-01	0.45287E-02		0.20950E-02	0.41016E-03	0.19087E-04	0.34194E-02	0.17484E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05D,	21/07/80,	1.4705	603.1	10.0066	0.9423E-01	716.37	0.17487			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.97090E+00		0.22534E-01	0.0		0.0	0.45667E-03	0.21764E-04	0.39929E-02	0.20909E-02	FEED
0.96917E+00		0.19050E-01	0.41847E-02		0.19592E-02	0.43651E-03	0.19796E-04	0.34561E-02	0.17222E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05E,	21/07/80,	1.4525	601.1	10.0066	0.8889E-01	694.45	0.13159			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.97731E+00		0.15738E-01	0.0		0.0	0.43300E-03	0.21313E-04	0.41946E-02	0.23060E-02	FEED
0.97594E+00		0.12901E-01	0.33608E-02		0.15904E-02	0.41898E-03	0.19883E-04	0.37728E-02	0.19997E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05G,	04/09/80,	1.4618	596.9	9.0041	0.6246E-01	945.33	0.19496			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.97267E+00		0.21003E-01	0.0		0.0	0.36926E-03	0.17997E-04	0.38007E-02	0.21419E-02	FEED
0.97069E+00		0.17232E-01	0.46087E-02		0.21492E-02	0.35090E-03	0.16172E-04	0.32293E-02	0.17208E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05F,	04/09/80,	1.4559	595.5	9.0041	0.4878E-01	1195.59	0.19088			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.97334E+00		0.20343E-01	0.0		0.0	0.35179E-03	0.17282E-04	0.37794E-02	0.21720E-02	FEED
0.97141E+00		0.16619E-01	0.45369E-02		0.21032E-02	0.33470E-03	0.15568E-04	0.32234E-02	0.17539E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05H,	23/10/80,	1.4758	591.1	1.5975	0.2669E-01	317.70	0.13415			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96479E+00	0.28147E-01	0.0	0.0	0.31813E-03	0.16462E-04	0.41305E-02	0.25943E-02	FEED		
0.96338E+00	0.25040E-01	0.36066E-02	0.17023E-02	0.30763E-03	0.15336E-04	0.37069E-02	0.22430E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05I,	24/10/80,	1.4810	592.1	1.5975	0.4412E-01	204.44	0.11289			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96202E+00	0.31215E-01	0.0	0.0	0.32527E-03	0.16511E-04	0.39851E-02	0.24346E-02	FEED		
0.96061E+00	0.29017E-01	0.27790E-02	0.14630E-02	0.31629E-03	0.15564E-04	0.36415E-02	0.21566E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05J,	05/11/80,	1.4793	592.6	0.6079	0.5498E-01	60.70	0.05416			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96893E+00	0.24115E-01	0.0	0.0	0.33322E-03	0.17021E-04	0.40942E-02	0.25065E-02	FEED		
0.96832E+00	0.22950E-01	0.13808E-02	0.70571E-03	0.32892E-03	0.16561E-04	0.39263E-02	0.23693E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI05K,	11/11/80,	1.4793	593.1	0.6079	0.4798E-01	79.51	0.06102			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96932E+00	0.24417E-01	0.0	0.0	0.32802E-03	0.16188E-04	0.37254E-02	0.21943E-02	FEED		
0.96859E+00	0.23363E-01	0.13667E-02	0.73208E-03	0.32321E-03	0.15693E-04	0.35530E-02	0.20589E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI06A,	24/07/80,	1.4688	603.1	10.0066	0.2341E-01	2119.83	0.15446			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97409E+00	0.17511E-01	0.0	0.0	0.49310E-03	0.25393E-04	0.50339E-02	0.28482E-02	FEED		
0.97194E+00	0.13651E-01	0.47898E-02	0.22773E-02	0.47448E-03	0.23386E-04	0.44372E-02	0.24030E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SIO6D,	25/07/80,	1.4631	603.1	10.0066	0.7280E-01	681.45	0.14295				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.97114E+00	0.20442E-01	0.0		0.0	0.49211E-03	0.25388E-04	0.50422E-02	0.28582E-02	FEED	
	0.96981E+00	0.16194E-01	0.44881E-02		0.20753E-02	0.47499E-03	0.23542E-04	0.44919E-02	0.24463E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SIO6B,	25/07/80,	1.4655	601.1	10.0066	0.3989E-01	1340.54	0.15756				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.97151E+00	0.20746E-01	0.0		0.0	0.45046E-03	0.22858E-04	0.46377E-02	0.26284E-02	FEED	
	0.97141E+00	0.15157E-01	0.45627E-02		0.21210E-02	0.43298E-03	0.21025E-04	0.40823E-02	0.22141E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SIO6C,	25/07/80,	1.4655	603.1	10.0066	0.4629E-01	1043.31	0.15953				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.97097E+00	0.20427E-01	0.0		0.0	0.49595E-03	0.25743E-04	0.51441E-02	0.29339E-02	FEED	
	0.96879E+00	0.16241E-01	0.51047E-02		0.23855E-02	0.47659E-03	0.23640E-04	0.45142E-02	0.24603E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SIO6E,	04/09/80,	1.4559	595.5	9.0041	0.3067E-01	1885.98	0.20173				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.97313E+00	0.20510E-01	0.0		0.0	0.35252E-03	0.17354E-04	0.38029E-02	0.21900E-02	FEED	
	0.97108E+00	0.16535E-01	0.48411E-02		0.22320E-02	0.33435E-03	0.15530E-04	0.32108E-02	0.17446E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SIO6G,	04/09/80,	1.4618	594.8	9.0041	0.4663E-01	884.26	0.14346				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.97248E+00	0.19217E-01	0.0		0.0	0.37513E-03	0.20085E-04	0.48518E-02	0.30565E-02	FEED	
	0.97049E+00	0.15529E-01	0.45603E-02		0.21100E-02	0.36205E-03	0.18615E-04	0.43185E-02	0.26127E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO6F,	04/09/80,	1.4595	594.8	9.0041	0.3651E-01	1131.60	0.15268			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97207E+00	0.19626E-01	0.0	0.0	0.37474E-03	0.20075E-04	0.48523E-02	0.30586E-02	FEED		
0.96908E+00	0.16587E-01	0.48405E-02	0.22505E-02	0.36077E-03	0.18502E-04	0.42814E-02	0.25836E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO6H,	05/09/80,	1.4609	592.1	9.0041	0.6875E-01	560.48	0.13374			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97132E+00	0.20111E-01	0.0	0.0	0.34647E-03	0.18983E-04	0.49452E-02	0.32609E-02	FEED		
0.96838E+00	0.17550E-01	0.44108E-02	0.20572E-02	0.33530E-03	0.17686E-04	0.44360E-02	0.28162E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO6I,	10/11/80,	1.4840	592.1	0.6079	0.2402E-01	119.85	0.09353			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96444E+00	0.27762E-01	0.0	0.0	0.34027E-03	0.18028E-04	0.45415E-02	0.28959E-02	FEED		
0.96332E+00	0.25402E-01	0.27400E-02	0.13483E-02	0.33264E-03	0.17179E-04	0.42184E-02	0.26220E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO6K,	11/11/80,	1.4793	591.1	0.6079	0.4837E-01	58.76	0.05022			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96686E+00	0.25320E-01	0.0	0.0	0.32875E-03	0.17535E-04	0.45349E-02	0.29358E-02	FEED		
0.96618E+00	0.24125E-01	0.14046E-02	0.79820E-03	0.32487E-03	0.17096E-04	0.43624E-02	0.27864E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO6J,	11/11/80,	1.4816	591.1	0.6079	0.3645E-01	74.81	0.07074			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96296E+00	0.28954E-01	0.0	0.0	0.33249E-03	0.17907E-04	0.46760E-02	0.30565E-02	FEED		
0.96205E+00	0.27125E-01	0.21056E-02	0.11142E-02	0.32693E-03	0.17273E-04	0.44250E-02	0.28376E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI06L,	12/11/80,	1.4797	591.1	0.6079	0.7233E-01	38.07	0.04059			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97220E+00	0.19773E-01	0.0	0.0	0.33143E-03	0.17816E-04	0.46436E-02	0.30297E-02	FEED		
0.97160E+00	0.18825E-01	0.11531E-02	0.67547E-03	0.32829E-03	0.17457E-04	0.45009E-02	0.29049E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08A,	26/07/80,	1.4613	598.4	10.0066	0.2804E-01	1234.68	0.10501			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97052E+00	0.18669E-01	0.0	0.0	0.45706E-03	0.26057E-04	0.62538E-02	0.40716E-02	FEED		
0.96863E+00	0.15140E-01	0.43008E-02	0.20703E-02	0.44593E-03	0.24686E-04	0.57529E-02	0.36369E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08B,	26/07/80,	1.4613	600.3	10.0066	0.3733E-01	983.74	0.10828			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97204E+00	0.17479E-01	0.0	0.0	0.48131E-03	0.26935E-04	0.61196E-02	0.38503E-02	FEED		
0.97015E+00	0.14001E-01	0.42715E-02	0.20464E-02	0.46915E-03	0.25471E-04	0.56140E-02	0.34267E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08D,	11/08/80,	1.4636	593.1	9.0041	0.2773E-01	1070.29	0.14149			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96869E+00	0.20586E-01	0.0	0.0	0.38381E-03	0.22375E-04	0.60826E-02	0.42321E-02	FEED		
0.96611E+00	0.15782E-01	0.58165E-02	0.28500E-02	0.37103E-03	0.20772E-04	0.54230E-02	0.36236E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08C,	11/08/80,	1.4554	599.1	9.0041	0.3684E-01	874.66	0.13227			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96946E+00	0.19930E-01	0.0	0.0	0.46353E-03	0.26221E-04	0.61611E-02	0.39571E-02	FEED		
0.96738E+00	0.15314E-01	0.52518E-02	0.26161E-02	0.44911E-03	0.24471E-04	0.55384E-02	0.34264E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8E,	11/08/80,	1.4636	593.1	9.0041	0.5809E-01	549.40	0.13824			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96956E+00	0.20333E-01	0.0		0.0	0.37697E-03	0.21588E-04	0.57649E-02	0.39401E-02	FEED
	0.96572E+00	0.17441E-01	0.52734E-02		0.26503E-02	0.36461E-03	0.20065E-04	0.51492E-02	0.33820E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8F,	13/08/80,	1.4635	598.4	9.0041	0.7269E-01	438.44	0.11716			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.97020E+00	0.19204E-01	0.0		0.0	0.45481E-03	0.25763E-04	0.61436E-02	0.39742E-02	FEED
	0.96806E+00	0.15412E-01	0.46066E-02		0.23572E-02	0.44235E-03	0.24243E-04	0.55935E-02	0.35009E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8H,	02/09/80,	1.4569	597.6	9.0041	0.5728E-01	564.57	0.12224			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96859E+00	0.20981E-01	0.0		0.0	0.43957E-03	0.24905E-04	0.60322E-02	0.39289E-02	FEED
	0.96651E+00	0.16966E-01	0.48838E-02		0.22817E-02	0.42695E-03	0.23370E-04	0.54687E-02	0.34412E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8G,	02/09/80,	1.4569	597.7	9.0041	0.3701E-01	867.11	0.13275			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96859E+00	0.20906E-01	0.0		0.0	0.44205E-03	0.25093E-04	0.60776E-02	0.39627E-02	FEED
	0.96591E+00	0.16917E-01	0.53211E-02		0.25189E-02	0.42822E-03	0.23406E-04	0.54587E-02	0.34271E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8I,	03/09/80,	1.4626	598.4	9.0041	0.7634E-01	441.98	0.11951			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.97023E+00	0.19660E-01	0.0		0.0	0.44815E-03	0.25033E-04	0.58865E-02	0.37550E-02	FEED
	0.96840E+00	0.15724E-01	0.46198E-02		0.21465E-02	0.43554E-03	0.23526E-04	0.53497E-02	0.33000E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8J,	11/09/80,	1.4673	595.9	5.0086	0.2999E-01	615.06	0.13276			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96750E+00	0.22495E-01	0.0		0.0	0.41280E-03	0.23240E-04	0.57792E-02	0.37934E-02	FEED
	0.96547E+00	0.18132E-01	0.51794E-02		0.23174E-02	0.39980E-03	0.21679E-04	0.51926E-02	0.32829E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8K,	28/09/80,	1.4609	593.1	5.0086	0.3780E-01	469.54	0.08872			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96949E+00	0.20413E-01	0.0		0.0	0.37642E-03	0.21565E-04	0.57614E-02	0.39394E-02	FEED
	0.96801E+00	0.17557E-01	0.34711E-02		0.16189E-02	0.36866E-03	0.20609E-04	0.53724E-02	0.35844E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8L,	28/09/80,	1.4609	593.1	5.0086	0.3780E-01	469.54	0.08872			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96949E+00	0.20413E-01	0.0		0.0	0.37642E-03	0.21565E-04	0.57614E-02	0.39394E-02	FEED
	0.96801E+00	0.17557E-01	0.34711E-02		0.16189E-02	0.36866E-03	0.20609E-04	0.53724E-02	0.35844E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8M,	30/09/80	1.4728	594.1	5.0086	0.5991E-01	309.96	0.09999			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96792E+00	0.22316E-01	0.0		0.0	0.38727E-03	0.21805E-04	0.56149E-02	0.37417E-02	FEED
	0.96610E+00	0.19436E-01	0.38041E-02		0.17116E-02	0.37819E-03	0.20709E-04	0.51863E-02	0.33612E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SIO8N,	02/10/80,	1.4684	593.1	5.0086	0.7255E-01	235.44	0.08642			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96960E+00	0.20014E-01	0.0		0.0	0.38103E-03	0.21982E-04	0.59138E-02	0.40719E-02	FEED
	0.96819E+00	0.17070E-01	0.35034E-02		0.16038E-02	0.37341E-03	0.21034E-04	0.55253E-02	0.37146E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08O,	02/10/80,	1.4681	593.1	5.0086	0.7259E-01	235.48	0.08770			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96825E+00	0.21379E-01	0.0	0.0	0.38084E-03	0.21965E-04	0.59073E-02	0.40662E-02	FEED		
0.96767E+00	0.17524E-01	0.35876E-02	0.16042E-02	0.37311E-03	0.21009E-04	0.55166E-02	0.37074E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08Q,	09/10/80,	1.4760	591.1	1.5975	0.2828E-01	188.49	0.08744			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96826E+00	0.21380E-01	0.0	0.0	0.35753E-03	0.20773E-04	0.58519E-02	0.41267E-02	FEED		
0.96680E+00	0.18428E-01	0.35659E-02	0.16144E-02	0.35030E-03	0.19866E-04	0.54627E-02	0.37602E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08R,	09/10/80,	1.4772	591.1	1.5975	0.3701E-01	147.81	0.08018			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96872E+00	0.21159E-01	0.0	0.0	0.35527E-03	0.20495E-04	0.57330E-02	0.40143E-02	FEED		
0.96812E+00	0.17790E-01	0.31970E-02	0.14502E-02	0.34868E-03	0.19681E-04	0.53863E-02	0.36901E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08S,	10/10/80,	1.4750	591.1	1.5975	0.7738E-01	74.96	0.05447			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97158E+00	0.18771E-01	0.0	0.0	0.34983E-03	0.19905E-04	0.54915E-02	0.37924E-02	FEED		
0.97061E+00	0.17191E-01	0.20222E-02	0.96695E-03	0.34545E-03	0.19367E-04	0.52645E-02	0.35823E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08T,	10/10/80,	1.4820	591.1	1.5975	0.5932E-01	96.92	0.06168			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97025E+00	0.20055E-01	0.0	0.0	0.35147E-03	0.19995E-04	0.55155E-02	0.38085E-02	FEED		
0.96928E+00	0.18122E-01	0.23522E-02	0.10506E-02	0.34646E-03	0.19382E-04	0.52576E-02	0.35700E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08U,	11/11/80,	1.4769	591.1	0.6079	0.2847E-01	71.89	0.05732			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96408E+00	0.25693E-01	0.0	0.0	0.35628E-03	0.20615E-04	0.57835E-02	0.40617E-02	FEED		
0.96869E+00	0.18112E-01	0.22255E-02	0.12048E-02	0.35164E-03	0.20069E-04	0.55537E-02	0.38472E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08V,	11/11/80,	1.4793	591.1	0.6079	0.3595E-01	56.01	0.04947			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96486E+00	0.24744E-01	0.0	0.0	0.35852E-03	0.20841E-04	0.58744E-02	0.41448E-02	FEED		
0.96398E+00	0.23123E-01	0.19125E-02	0.10238E-02	0.35448E-03	0.20331E-04	0.56542E-02	0.39362E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI08W,	12/11/80,	1.4822	593.1	0.6079	0.5602E-01	37.05	0.04017			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96863E+00	0.21059E-01	0.0	0.0	0.38263E-03	0.21961E-04	0.58779E-02	0.40265E-02	FEED		
0.96791E+00	0.19785E-01	0.15374E-02	0.80937E-03	0.37913E-03	0.21526E-04	0.56991E-02	0.38619E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10A,	11/08/80,	1.4685	593.1	9.0041	0.2416E-01	789.24	0.10324			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96381E+00	0.20701E-01	0.0	0.0	0.42976E-03	0.27929E-04	0.84641E-02	0.65651E-02	FEED		
0.96110E+00	0.15497E-01	0.63105E-02	0.29757E-02	0.42015E-03	0.26505E-04	0.77972E-02	0.58707E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10B,	12/08/80,	1.4671	596.9	9.0041	0.3757E-01	526.45	0.10741			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96630E+00	0.18137E-01	0.0	0.0	0.48755E-03	0.31194E-04	0.86475E-02	0.63973E-02	FEED		
0.96044E+00	0.15933E-01	0.65704E-02	0.29568E-02	0.47614E-03	0.29504E-04	0.79214E-02	0.56755E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10C,	13/08/80.	1.4659	598.4	9.0041	0.4957E-01	412.55	0.09704			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96478E+00	0.19921E-01	0.0	0.0	0.50906E-03	0.32188E-04	0.85680E-02	0.61868E-02	FEED	
	0.96222E+00	0.15260E-01	0.56589E-02	0.28246E-02	0.49831E-03	0.30644E-04	0.79336E-02	0.55716E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10D,	15/08/80	1.4580	595.5	9.0041	0.7881E-01	262.65	0.08903			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96547E+00	0.19707E-01	0.0	0.0	0.45685E-03	0.29045E-04	0.82201E-02	0.61137E-02	FEED	
	0.96313E+00	0.15587E-01	0.49943E-02	0.25973E-02	0.44798E-03	0.27769E-04	0.76620E-02	0.55559E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10E,	19/08/80.	1.4601	595.5	9.0041	0.2499E-01	804.12	0.09824			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96412E+00	0.20730E-01	0.0	0.0	0.46038E-03	0.29452E-04	0.83869E-02	0.62765E-02	FEED	
	0.96365E+00	0.13809E-01	0.57112E-02	0.29190E-02	0.45063E-03	0.28046E-04	0.77701E-02	0.56572E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10F,	19/80/80.	1.4556	595.5	9.0041	0.3854E-01	522.81	0.09240			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96660E+00	0.18219E-01	0.0	0.0	0.45969E-03	0.29453E-04	0.84003E-02	0.62962E-02	FEED	
	0.96348E+00	0.14466E-01	0.53456E-02	0.27239E-02	0.45047E-03	0.28104E-04	0.78047E-02	0.56961E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10G,	20/08/80.	1.4613	628.4	9.0041	0.5349E-01	514.61	0.09764			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96479E+00	0.19340E-01	0.0	0.0	0.12883E-02	0.71675E-04	0.96703E-02	0.48416E-02	FEED	
	0.96219E+00	0.15168E-01	0.53109E-02	0.26937E-02	0.12605E-02	0.68204E-04	0.89488E-02	0.43571E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10H,	21/08/80.	1.4692	595.5	9.0041	0.7916E-01	263.44	0.08150			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96816E+00	0.17185E-01	0.0	0.0	0.45772E-03	0.28936E-04	0.81425E-02	0.60216E-02	FEED		
0.96598E+00	0.13523E-01	0.45438E-02	0.23160E-02	0.44960E-03	0.27773E-04	0.76366E-02	0.55183E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10I,	26/08/80.	1.4647	595.5	9.0041	0.2615E-01	1077.71	0.12111			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96840E+00	0.20172E-01	0.0	0.0	0.42373E-03	0.24892E-04	0.65091E-02	0.44730E-02	FEED		
0.96551E+00	0.16371E-01	0.54458E-02	0.24141E-02	0.41184E-03	0.23372E-04	0.59042E-02	0.39196E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10K,	30/09/80.	1.4669	593.1	5.0086	0.3948E-01	288.23	0.07083			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96395E+00	0.21451E-01	0.0	0.0	0.42188E-03	0.26948E-04	0.80272E-02	0.61197E-02	FEED		
0.96225E+00	0.18057E-01	0.40988E-02	0.18840E-02	0.41538E-03	0.26010E-04	0.75951E-02	0.56762E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10J,	30/09/80.	1.4681	593.1	5.0086	0.2593E-01	443.67	0.07280			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96397E+00	0.21579E-01	0.0	0.0	0.42088E-03	0.26801E-04	0.79583E-02	0.60483E-02	FEED		
0.96223E+00	0.18132E-01	0.41619E-02	0.19246E-02	0.41421E-03	0.25841E-04	0.75179E-02	0.55979E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10L,	30/09/80.	1.4669	594.1	5.0086	0.5144E-01	224.63	0.06969			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96388E+00	0.21586E-01	0.0	0.0	0.43552E-03	0.27656E-04	0.80321E-02	0.60367E-02	FEED		
0.96219E+00	0.18303E-01	0.40299E-02	0.18113E-02	0.42892E-03	0.26709E-04	0.76067E-02	0.56062E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10N,	02/10/80,	1.4752	593.1	5.0086	0.7817E-01	144.25	0.06676			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96462E+00		0.20732E-01	0.0		0.0	0.42403E-03	0.27071E-04	0.80596E-02	0.61412E-02	FEED
0.96300E+00		0.17522E-01	0.38937E-02		0.17644E-02	0.41790E-03	0.26185E-04	0.76509E-02	0.57216E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10M,	02/10/80,	1.4681	593.1	5.0086	0.5104E-01	223.01	0.07620			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96242E+00		0.22994E-01	0.0		0.0	0.42203E-03	0.26946E-04	0.80229E-02	0.61137E-02	FEED
0.96062E+00		0.19310E-01	0.44076E-02		0.20256E-02	0.41502E-03	0.25936E-04	0.75581E-02	0.56373E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10P,	10/10/80,	1.4750	591.1	1.5975	0.4991E-01	70.12	0.05086			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96409E+00		0.21178E-01	0.0		0.0	0.39731E-03	0.25644E-04	0.80255E-02	0.62872E-02	FEED
0.96307E+00		0.18469E-01	0.29705E-02		0.13931E-02	0.39296E-03	0.25009E-04	0.77171E-02	0.59611E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10Q,	10/10/80,	1.4820	591.1	1.5975	0.7929E-01	45.60	0.04327			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96624E+00		0.19474E-01	0.0		0.0	0.39499E-03	0.25227E-04	0.78122E-02	0.60560E-02	FEED
0.96519E+00		0.17462E-01	0.24538E-02		0.11337E-02	0.39130E-03	0.24694E-04	0.75560E-02	0.57877E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10O,	10/10/80,	1.4820	591.1	1.5975	0.3808E-01	90.58	0.06182			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.96199E+00		0.23135E-01	0.0		0.0	0.39977E-03	0.25838E-04	0.80970E-02	0.63518E-02	FEED
0.96048E+00		0.20087E-01	0.36393E-02		0.17120E-02	0.39444E-03	0.25055E-04	0.77169E-02	0.59497E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10S,	04/11/80,	1.4794	591.1	0.6079	0.2709E-01	53.65	0.05608			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.95741E+00	0.28935E-01	0.0		0.0	0.38918E-03	0.24538E-04	0.75015E-02	0.57407E-02	FEED
	0.95680E+00	0.25739E-01	0.29412E-02		0.15101E-02	0.38438E-03	0.23867E-04	0.71856E-02	0.54153E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10R,	24/10/80	1.4397	591.1	1.5975	0.2091E-01	178.71	0.06970			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.95969E+00	0.26130E-01	0.0		0.0	0.38618E-03	0.24822E-04	0.77362E-02	0.60355E-02	FEED
	0.95806E+00	0.22847E-01	0.38489E-02		0.19032E-02	0.38029E-03	0.23971E-04	0.73265E-02	0.56054E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10U,	05/11/80,	1.4597	594.6	0.6079	0.5391E-01	27.51	0.03038			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.96389E+00	0.22145E-01	0.0		0.0	0.43597E-03	0.27335E-04	0.77630E-02	0.57368E-02	FEED
	0.96315E+00	0.20808E-01	0.16019E-02		0.83258E-03	0.43310E-03	0.26930E-04	0.75844E-02	0.55582E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI10T,	06/11/80,	1.4585	591.1	0.6079	0.4158E-01	34.76	0.04138			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.95839E+00	0.27753E-01	0.0		0.0	0.38701E-03	0.24611E-04	0.75887E-02	0.58575E-02	FEED
	0.95746E+00	0.25847E-01	0.22081E-02		0.11181E-02	0.38353E-03	0.24113E-04	0.73509E-02	0.56096E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15A,	13/08/80,	1.4760	598.4	9.0041	0.2794E-01	509.65	0.08177			
	N2	WATER	H2S		SO2	S2	S4	S6	S8	
	0.95976E+00	0.19609E-01	0.0		0.0	0.55971E-03	0.38599E-04	0.11206E-01	0.88257E-02	FEED
	0.95686E+00	0.14200E-01	0.66040E-02		0.31583E-02	0.55060E-03	0.37072E-04	0.10508E-01	0.80796E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15B,	15/08/80.	1.4664	596.9	9.0041	0.3594E-01	389.67	0.08763			
N2		WATER	H2S	SO2		S2	S4	S6	S8	
0.95786E+00		0.21378E-01	0.0	0.0		0.53147E-03	0.37039E-04	0.11185E-01	0.90129E-02	FEED
0.95473E+00		0.15501E-01	0.71070E-02	0.34758E-02		0.52220E-03	0.35467E-04	0.10437E-01	0.81963E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15C,	15/08/80.	1.4681	596.9	9.0041	0.5813E-01	253.80	0.07560			
N2		WATER	H2S	SO2		S2	S4	S6	S8	
0.95927E+00		0.20893E-01	0.0	0.0		0.52469E-03	0.36068E-04	0.10742E-01	0.85385E-02	FEED
0.95705E+00		0.15683E-01	0.57951E-02	0.29208E-02		0.51671E-03	0.34751E-04	0.10126E-01	0.78747E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15D,	20/08/80.	1.4665	593.1	9.0041	0.2831E-01	493.80	0.07925			
N2		WATER	H2S	SO2		S2	S4	S6	S8	
0.96067E+00		0.19172E-01	0.0	0.0		0.46454E-03	0.32641E-04	0.10696E-01	0.89698E-02	FEED
0.95783E+00		0.14023E-01	0.63364E-02	0.30362E-02		0.45720E-03	0.31389E-04	0.10049E-01	0.82346E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15E,	21/08/80.	1.4715	598.4	9.0041	0.3563E-01	393.10	0.08293			
N2		WATER	H2S	SO2		S2	S4	S6	S8	
0.95860E+00		0.20429E-01	0.0	0.0		0.56127E-03	0.38929E-04	0.11367E-01	0.90036E-02	FEED
0.95561E+00		0.14846E-01	0.67971E-02	0.32768E-02		0.55204E-03	0.37367E-04	0.10648E-01	0.82312E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15F,	21/08/80.	1.4692	595.5	9.0041	0.5924E-01	252.39	0.07607			
N2		WATER	H2S	SO2		S2	S4	S6	S8	
0.96071E+00		0.19893E-01	0.0	0.0		0.49788E-03	0.34200E-04	0.10457E-01	0.84030E-02	FEED
0.95806E+00		0.15241E-01	0.57252E-02	0.28567E-02		0.49021E-03	0.32936E-04	0.98506E-02	0.77423E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15G,	30/09/80,	1.4669	593.1	5.0086	0.2882E-01	275.43	0.06131			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.95667E+00	0.23538E-01	0.0	0.0	0.46207E-03	0.32290E-04	0.10522E-01	0.87761E-02	FEED	
	0.95477E+00	0.19372E-01	0.48400E-02	0.22783E-02	0.45638E-03	0.31335E-04	0.10033E-01	0.82217E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15H,	30/09/80,	1.4634	593.1	5.0086	0.3770E-01	213.27	0.05741			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.95828E+00	0.22116E-01	0.0	0.0	0.46000E-03	0.32080E-04	0.10433E-01	0.86840E-02	FEED	
	0.95641E+00	0.18356E-01	0.45248E-02	0.20735E-02	0.45469E-03	0.31192E-04	0.99781E-02	0.81695E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15I,	02/10/80,	1.4752	593.1	5.0086	0.5913E-01	138.53	0.06864			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.95781E+00	0.22999E-01	0.0	0.0	0.45969E-03	0.31783E-04	0.10248E-01	0.84563E-02	FEED	
	0.95580E+00	0.19400E-01	0.45499E-02	0.20356E-02	0.45423E-03	0.30880E-04	0.97900E-02	0.79437E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15J,	09/10/80,	1.4772	591.1	1.5975	0.1875E-01	133.69	0.05756			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.95729E+00	0.23173E-01	0.0	0.0	0.43262E-03	0.30326E-04	0.10307E-01	0.87699E-02	FEED	
	0.95541E+00	0.19402E-01	0.45074E-02	0.21158E-02	0.42761E-03	0.29483E-04	0.98568E-02	0.82489E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15K,	09/10/80,	1.4783	591.1	1.5975	0.2834E-01	86.81	0.05543			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.95621E+00	0.23948E-01	0.0	0.0	0.43485E-03	0.30613E-04	0.10450E-01	0.89288E-02	FEED	
	0.95440E+00	0.20230E-01	0.44254E-02	0.20556E-02	0.43002E-03	0.29795E-04	0.10010E-01	0.84180E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15M,	10/10/80,	1.4820	591.1	1.5975	0.5847E-01	43.66	0.04405			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95649E+00	0.24319E-01	0.0	0.0	0.43129E-03	0.30044E-04	0.10148E-01	0.85797E-02	FEED		
0.95522E+00	0.21349E-01	0.33874E-02	0.15879E-02	0.42745E-03	0.29407E-04	0.98093E-02	0.81908E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15L,	10/10/80,	1.4797	591.1	1.5975	0.3717E-01	67.30	0.04725			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95789E+00	0.22564E-01	0.0	0.0	0.43320E-03	0.30356E-04	0.10314E-01	0.87723E-02	FEED		
0.95636E+00	0.19450E-01	0.37307E-02	0.17071E-02	0.42909E-03	0.29665E-04	0.99443E-02	0.83445E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15N,	04/11/80,	1.4692	592.1	0.6079	0.1835E-01	50.94	0.03792			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95700E+00	0.22886E-01	0.0	0.0	0.44950E-03	0.31685E-04	0.10620E-01	0.90104E-02	FEED		
0.95573E+00	0.20340E-01	0.29740E-02	0.15092E-02	0.44611E-03	0.31109E-04	0.10315E-01	0.86572E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15O,	05/11/80,	1.4742	594.1	0.6079	0.2885E-01	33.68	0.04545			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.94906E+00	0.31207E-01	0.0	0.0	0.47895E-03	0.33242E-04	0.10552E-01	0.86683E-02	FEED		
0.94770E+00	0.28098E-01	0.35411E-02	0.17038E-02	0.47456E-03	0.32515E-04	0.10189E-01	0.82625E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15Q,	06/11/80,	1.4618	591.1	0.6079	0.5685E-01	16.49	0.02474			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95583E+00	0.24200E-01	0.0	0.0	0.43217E-03	0.30580E-04	0.10492E-01	0.90106E-02	FEED		
0.95498E+00	0.22572E-01	0.19314E-02	0.97766E-03	0.43005E-03	0.30217E-04	0.10295E-01	0.87799E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI15P,	06/11/80,	1.4597	591.1	0.6079	0.3591E-01	25.40	0.03121			
N2		WATER	H2S	SO2	S2	S4	S6	S8		
0.95226E+00		0.27280E-01	0.0	0.0	0.43489E-03	0.31007E-04	0.10719E-01	0.92762E-02	FEED	
0.95123E+00		0.25094E-01	0.25331E-02	0.12356E-02	0.43221E-03	0.30543E-04	0.10466E-01	0.89770E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI20A,	05/11/80,	1.4648	592.1	0.6079	0.2165E-01	31.96	0.03673			
N2		WATER	H2S	SO2	S2	S4	S6	S8		
0.94775E+00		0.26142E-01	0.0	0.0	0.48461E-03	0.36892E-04	0.13354E-01	0.12235E-01	FEED	
0.94443E+00		0.24706E-01	0.38695E-02	0.17636E-02	0.48143E-03	0.36232E-04	0.12966E-01	0.11745E-01	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI20C,	06/11/80,	1.4523	591.1	0.6079	0.4983E-01	15.85	0.02271			
N2		WATER	H2S	SO2	S2	S4	S6	S8		
0.94720E+00		0.26342E-01	0.0	0.0	0.46757E-03	0.35977E-04	0.13422E-01	0.12535E-01	FEED	
0.94546E+00		0.25070E-01	0.23883E-02	0.11660E-02	0.46568E-03	0.35585E-04	0.13184E-01	0.12228E-01	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI20B,	06/11/80,	1.4597	591.1	0.6079	0.2715E-01	24.47	0.03271			
N2		WATER	H2S	SO2	S2	S4	S6	S8		
0.94492E+00		0.28231E-01	0.0	0.0	0.47125E-03	0.36360E-04	0.13602E-01	0.12738E-01	FEED	
0.94357E+00		0.25121E-01	0.35435E-02	0.16936E-02	0.46850E-03	0.35801E-04	0.13265E-01	0.12304E-01	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI25A,	12/11/80,	1.4832	591.1	0.6079	0.1896E-01	31.35	0.03364			
N2		WATER	H2S	SO2	S2	S4	S6	S8		
0.94700E+00		0.23777E-01	0.0	0.0	0.48868E-03	0.38459E-04	0.14676E-01	0.14018E-01	FEED	
0.94536E+00		0.20426E-01	0.39801E-02	0.18876E-02	0.48588E-03	0.37855E-04	0.14300E-01	0.13523E-01	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SI25B,	12/11/80,	1.3477	591.1	0.6079	0.2423E-01	23.64	0.01661				
	N2	WATER	H2S	SO2	S2	S4	S6	S8			
	0.94452E+00	0.23123E-01	0.0	0.0	0.47042E-03	0.39197E-04	0.15836E-01	0.16016E-01	FEED		
	0.94235E+00	0.22627E-01	0.20839E-02	0.10986E-02	0.46920E-03	0.38882E-04	0.15623E-01	0.15714E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SI25C,	13/11/80,	1.4756	593.1	0.6079	0.3981E-01	15.94	0.02324				
	N2	WATER	H2S	SO2	S2	S4	S6	S8			
	0.94528E+00	0.26590E-01	0.0	0.0	0.51499E-03	0.39802E-04	0.14345E-01	0.13233E-01	FEED		
	0.94422E+00	0.24347E-01	0.26292E-02	0.12503E-02	0.51289E-03	0.39370E-04	0.14092E-01	0.12911E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SI30A,	12/11/80,	1.4832	591.1	0.6079	0.1562E-01	30.60	0.03062				
	N2	WATER	H2S	SO2	S2	S4	S6	S8			
	0.93929E+00	0.25436E-01	0.0	0.0	0.51650E-03	0.42910E-04	0.17285E-01	0.17430E-01	FEED		
	0.93751E+00	0.21711E-01	0.43801E-02	0.21001E-02	0.51410E-03	0.42309E-04	0.16883E-01	0.16864E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SI30B,	13/11/80,	1.4815	592.1	0.6079	0.1983E-01	23.74	0.02952				
	N2	WATER	H2S	SO2	S2	S4	S6	S8			
	0.94226E+00	0.21694E-01	0.0	0.0	0.53722E-03	0.44735E-04	0.17713E-01	0.17752E-01	FEED		
	0.94044E+00	0.18100E-01	0.43220E-02	0.20477E-02	0.53486E-03	0.44132E-04	0.17315E-01	0.17195E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
SI30C,	13/11/80,	1.4827	593.1	0.6079	0.3087E-01	15.45	0.02239				
	N2	WATER	H2S	SO2	S2	S4	S6	S8			
	0.94481E+00	0.19308E-01	0.0	0.0	0.55517E-03	0.45963E-04	0.17745E-01	0.17534E-01	FEED		
	0.94322E+00	0.16837E-01	0.31782E-02	0.16088E-02	0.55330E-03	0.45489E-04	0.17440E-01	0.17113E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI35A,	13/11/80,	1.4768	593.1	0.6079	0.2701E-01	15.19	0.02182			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93479E+00	0.24213E-01	0.0	0.0	0.57575E-03	0.49581E-04	0.19910E-01	0.20464E-01	FEED		
0.93329E+00	0.21167E-01	0.35996E-02	0.17613E-02	0.57404E-03	0.49094E-04	0.19579E-01	0.19985E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI35B,	13/11/80,	1.4791	593.1	0.6079	0.1760E-01	23.51	0.02679			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93403E+00	0.25302E-01	0.0	0.0	0.57502E-03	0.49380E-04	0.19775E-01	0.20267E-01	FEED		
0.93225E+00	0.21539E-01	0.44312E-02	0.20969E-02	0.57293E-03	0.48785E-04	0.19372E-01	0.19687E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
SI35C,	13/11/80,	1.4768	593.1	0.6079	0.1416E-01	30.52	0.02803			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93298E+00	0.27816E-01	0.0	0.0	0.56821E-03	0.48307E-04	0.19152E-01	0.19433E-01	FEED		
0.93124E+00	0.23964E-01	0.44647E-02	0.21183E-02	0.56596E-03	0.47695E-04	0.18744E-01	0.18853E-01	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO1A	,19/11/80,	1.4738	593.1	0.6079	0.1547E-01	47.53	0.13573			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97655E+00	0.11436E-01	0.0	0.0	0.39918E-03	0.24029E-04	0.67450E-02	0.48459E-02	FEED		
0.97550E+00	0.98734E-02	0.19345E-02	0.11385E-02	0.39521E-03	0.23499E-04	0.65158E-02	0.46240E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO1B	,20/11/80,	1.4711	592.1	0.6079	0.2435E-01	35.17	0.11139			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97815E+00	0.98154E-02	0.0	0.0	0.38582E-03	0.23356E-04	0.67227E-02	0.48981E-02	FEED		
0.97744E+00	0.87156E-02	0.13746E-02	0.76018E-03	0.38318E-03	0.23001E-04	0.65649E-02	0.47429E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO1C	,25/11/80,	1.4648	591.1	0.6079	0.3068E-01	27.69	0.11148			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97786E+00	0.99181E-02	0.0	0.0	0.37384E-03	0.22874E-04	0.67863E-02	0.50399E-02	FEED		
0.97712E+00	0.88058E-02	0.13898E-02	0.77713E-03	0.37131E-03	0.22529E-04	0.66278E-02	0.48809E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO1D	,02/12/80,	1.4753	593.1	0.6079	0.4631E-01	17.46	0.09576			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97719E+00	0.10381E-01	0.0	0.0	0.40363E-03	0.24540E-04	0.69573E-02	0.50484E-02	FEED		
0.97657E+00	0.93807E-02	0.12451E-02	0.65229E-03	0.40127E-03	0.24219E-04	0.68168E-02	0.49106E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO1E	,04/12/80,	1.4761	591.1	0.6079	0.6025E-01	13.78	0.08434			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97766E+00	0.10070E-01	0.0	0.0	0.37628E-03	0.22996E-04	0.68143E-02	0.50547E-02	FEED		
0.97730E+00	0.92174E-02	0.91088E-03	0.51059E-03	0.37462E-03	0.22770E-04	0.67110E-02	0.49511E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI01F	,12/12/80,	1.4709	591.1	0.6079	0.2349E-01	36.39	0.12085			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.97776E+00	0.98188E-02	0.0	0.0	0.37670E-03	0.23129E-04	0.68854E-02	0.51311E-02	FEED	
	0.97706E+00	0.86260E-02	0.15400E-02	0.68206E-03	0.37413E-03	0.22777E-04	0.67234E-02	0.49681E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02A	,17/11/80,	1.4714	593.1	0.6079	0.1534E-01	24.55	0.12429			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96550E+00	0.22368E-01	0.0	0.0	0.39993E-03	0.24157E-04	0.68046E-02	0.49057E-02	FEED	
	0.96405E+00	0.19559E-01	0.32358E-02	0.17595E-02	0.39347E-03	0.23298E-04	0.64333E-02	0.45465E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02B	,20/11/80,	1.4613	593.1	0.6079	0.2401E-01	19.47	0.10443			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96955E+00	0.18135E-01	0.0	0.0	0.39974E-03	0.24301E-04	0.68888E-02	0.49982E-02	FEED	
	0.96866E+00	0.16226E-01	0.21898E-02	0.10921E-02	0.39561E-03	0.23746E-04	0.66465E-02	0.47614E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02C	,24/11/80,	1.4731	592.1	0.6079	0.3042E-01	14.25	0.09618			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96833E+00	0.19366E-01	0.0	0.0	0.38881E-03	0.23687E-04	0.68613E-02	0.50309E-02	FEED	
	0.96737E+00	0.17486E-01	0.22113E-02	0.11168E-02	0.38475E-03	0.23139E-04	0.66167E-02	0.47893E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02D	,03/12/80,	1.4723	591.1	0.6079	0.4680E-01	9.84	0.07568			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.96954E+00	0.18204E-01	0.0	0.0	0.37548E-03	0.22958E-04	0.68061E-02	0.50509E-02	FEED	
	0.96863E+00	0.16810E-01	0.16828E-02	0.10202E-02	0.37229E-03	0.22525E-04	0.66081E-02	0.48527E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02E	,04/12/80,	1.4761	593.1	0.6079	0.6048E-01	6.90	0.05877			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96759E+00	0.20106E-01	0.0	0.0	0.40254E-03	0.24395E-04	0.68940E-02	0.49864E-02	FEED		
0.96703E+00	0.18914E-01	0.13938E-02	0.65419E-03	0.39996E-03	0.24048E-04	0.67427E-02	0.48387E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02F	,12/12/80,	1.4721	591.1	0.6079	0.2343E-01	19.63	0.09873			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.96933E+00	0.18234E-01	0.0	0.0	0.37711E-03	0.23160E-04	0.68968E-02	0.51411E-02	FEED		
0.96833E+00	0.16416E-01	0.22077E-02	0.10938E-02	0.37326E-03	0.22636E-04	0.66561E-02	0.48993E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI02G	,12/12/80,	1.4697	591.1	0.6079	0.2953E-01	14.92	0.09950			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.97096E+00	0.19071E-01	0.0	0.0	0.35238E-03	0.20267E-04	0.56518E-02	0.39454E-02	FEED		
0.96996E+00	0.17156E-01	0.23294E-02	0.10840E-02	0.34752E-03	0.19663E-04	0.53944E-02	0.37046E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI04A	,19/11/80,	1.4738	593.1	0.6079	0.1532E-01	13.91	0.11038			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.94838E+00	0.39481E-01	0.0	0.0	0.40040E-03	0.24176E-04	0.68069E-02	0.49052E-02	FEED		
0.94660E+00	0.35057E-01	0.46474E-02	0.26307E-02	0.39083E-03	0.22916E-04	0.62660E-02	0.43850E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI04B	,20/11/80,	1.4652	592.1	0.6079	0.2424E-01	10.25	0.09644			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95387E+00	0.33993E-01	0.0	0.0	0.38574E-03	0.23439E-04	0.67723E-02	0.49529E-02	FEED		
0.95262E+00	0.30674E-01	0.36150E-02	0.17392E-02	0.37905E-03	0.22550E-04	0.63789E-02	0.45674E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI04C	,24/11/80,	1.4731	591.1	0.6079	0.3033E-01	7.44	0.08381			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95053E+00	0.37166E-01	0.0	0.0	0.37604E-03	0.23015E-04	0.68295E-02	0.50732E-02	FEED		
0.94941E+00	0.34011E-01	0.33776E-02	0.16381E-02	0.37007E-03	0.22212E-04	0.64645E-02	0.47095E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI04D	,03/12/80,	1.4723	593.1	0.6079	0.4662E-01	5.46	0.06358			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95460E+00	0.33023E-01	0.0	0.0	0.40252E-03	0.24455E-04	0.69284E-02	0.50239E-02	FEED		
0.95384E+00	0.30899E-01	0.23070E-02	0.10678E-02	0.39826E-03	0.23885E-04	0.66799E-02	0.47815E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI04E	,04/11/80,	1.4761	593.1	0.6079	0.5970E-01	3.84	0.05012			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.95090E+00	0.36638E-01	0.0	0.0	0.40409E-03	0.24581E-04	0.69731E-02	0.50628E-02	FEED		
0.95009E+00	0.34772E-01	0.20983E-02	0.10329E-02	0.40015E-03	0.24053E-04	0.67421E-02	0.48369E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06A	,20/11/80,	1.4648	591.1	0.6079	0.1538E-01	9.49	0.11416			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93012E+00	0.57800E-01	0.0	0.0	0.37250E-03	0.22711E-04	0.67140E-02	0.49685E-02	FEED		
0.92850E+00	0.51112E-01	0.66044E-02	0.31232E-02	0.36044E-03	0.21126E-04	0.60039E-02	0.42712E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06B	,22/11/80,	1.4531	591.1	0.6079	0.2376E-01	6.57	0.09410			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93326E+00	0.54334E-01	0.0	0.0	0.37339E-03	0.23002E-04	0.68705E-02	0.51371E-02	FEED		
0.93353E+00	0.49235E-01	0.37886E-02	0.18505E-02	0.36677E-03	0.22123E-04	0.64704E-02	0.47372E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06C	,25/11/80,	1.4743	591.1	0.6079	0.3046E-01	5.10	0.04214			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.93384E+00		0.53927E-01	0.0		0.0	0.37563E-03	0.22946E-04	0.67963E-02	0.50391E-02	FEED
0.93322E+00		0.51620E-01	0.22918E-02		0.11339E-02	0.37155E-03	0.22400E-04	0.65480E-02	0.47915E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06D	,03/12/80,	1.4664	593.1	0.6079	0.4621E-01	3.45	0.05878			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.93453E+00		0.52939E-01	0.0		0.0	0.40290E-03	0.24598E-04	0.70034E-02	0.51033E-02	FEED
0.93367E+00		0.49781E-01	0.32934E-02		0.14133E-02	0.39699E-03	0.23808E-04	0.66583E-02	0.47659E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06E	,04/12/80,	1.4702	593.1	0.6079	0.5962E-01	2.52	0.04911			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.93131E+00		0.56162E-01	0.0		0.0	0.40353E-03	0.24612E-04	0.70000E-02	0.50956E-02	FEED
0.93075E+00		0.53371E-01	0.27672E-02		0.11650E-02	0.39860E-03	0.23954E-04	0.67127E-02	0.48146E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06F	,12/12/80,	1.4709	591.1	0.6079	0.2350E-01	6.30	0.06265			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.93082E+00		0.56752E-01	0.0		0.0	0.37679E-03	0.23140E-04	0.68903E-02	0.51360E-02	FEED
0.92899E+00		0.53092E-01	0.44274E-02		0.20132E-02	0.36913E-03	0.22106E-04	0.64192E-02	0.46661E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI06Fr	,12/12/80,	1.4697	591.1	0.6079	0.2981E-01	5.71	0.06596			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.93809E+00		0.49378E-01	0.0		0.0	0.37754E-03	0.23250E-04	0.69425E-02	0.51893E-02	FEED
0.93701E+00		0.46068E-01	0.34534E-02		0.16851E-02	0.37153E-03	0.22437E-04	0.65702E-02	0.48160E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO8A	,20/11/80,	1.4652	591.1	0.6079	0.1534E-01	7.78	0.09029			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.91722E+00		0.70672E-01	0.0		0.0	0.37282E-03	0.22743E-04	0.67273E-02	0.49812E-02	FEED
0.91538E+00		0.64162E-01	0.66593E-02		0.31307E-02	0.36067E-03	0.21146E-04	0.60113E-02	0.42777E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO8B	,22/11/80,	1.4519	591.1	0.6079	0.2362E-01	5.29	0.07834			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.91946E+00		0.68031E-01	0.0		0.0	0.37408E-03	0.23106E-04	0.69198E-02	0.51876E-02	FEED
0.91839E+00		0.62629E-01	0.51650E-02		0.24115E-02	0.36515E-03	0.21908E-04	0.63731E-02	0.46410E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO8C	,25/11/80,	1.4731	591.1	0.6079	0.3049E-01	3.52	0.04520			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.90968E+00		0.78088E-01	0.0		0.0	0.37541E-03	0.22938E-04	0.67953E-02	0.50394E-02	FEED
0.90910E+00		0.74511E-01	0.32831E-02		0.15792E-02	0.36957E-03	0.22162E-04	0.64440E-02	0.46903E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO8D	,03/12/80,	1.4688	593.1	0.6079	0.4208E-01	2.59	0.05138			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.90881E+00		0.77498E-01	0.0		0.0	0.41424E-03	0.25954E-04	0.75833E-02	0.56708E-02	FEED
0.90813E+00		0.73461E-01	0.37514E-02		0.17624E-02	0.40783E-03	0.25070E-04	0.71865E-02	0.52725E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WIO8E	,04/12/80,	1.4773	593.1	0.6079	0.5945E-01	1.86	0.04358			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.91167E+00		0.75824E-01	0.0		0.0	0.40471E-03	0.24637E-04	0.69941E-02	0.50818E-02	FEED
0.91098E+00		0.72464E-01	0.31157E-02		0.16285E-02	0.39869E-03	0.23838E-04	0.66467E-02	0.47432E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI08F	,12/12/80,	1.4697	591.1	0.6079	0.2994E-01	3.71	0.06405			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.91186E+00		0.75663E-01	0.0		0.0	0.37707E-03	0.23192E-04	0.69164E-02	0.51633E-02	FEED
0.91086E+00		0.70740E-01	0.47276E-02		0.21989E-02	0.36883E-03	0.22091E-04	0.64157E-02	0.46641E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI10A	,20/11/80,	1.4628	592.1	0.6079	0.1522E-01	6.34	0.11130			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.90003E+00		0.87717E-01	0.0		0.0	0.38640E-03	0.23557E-04	0.68288E-02	0.50108E-02	FEED
0.89866E+00		0.77835E-01	0.90774E-02		0.40978E-02	0.36933E-03	0.21341E-04	0.58633E-02	0.40776E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI10B	,22/11/80,	1.4531	591.1	0.6079	0.2356E-01	3.98	0.07024			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.89677E+00		0.90704E-01	0.0		0.0	0.37446E-03	0.23134E-04	0.69295E-02	0.51960E-02	FEED
0.89589E+00		0.84249E-01	0.58572E-02		0.27284E-02	0.36428E-03	0.21775E-04	0.63113E-02	0.45791E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI10C	,25/11/80,	1.4648	593.1	0.6079	0.3042E-01	2.93	0.03695			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.89261E+00		0.94982E-01	0.0		0.0	0.40132E-03	0.24434E-04	0.69371E-02	0.50408E-02	FEED
0.89214E+00		0.91424E-01	0.31888E-02		0.15319E-02	0.39533E-03	0.23641E-04	0.65926E-02	0.47053E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI10D	,03/12/80,	1.4747	592.1	0.6079	0.4564E-01	1.91	0.04456			
N2		WATER	H2S		SO2	S2	S4	S6	S8	
0.89124E+00		0.96183E-01	0.0		0.0	0.39164E-03	0.24005E-04	0.69963E-02	0.51613E-02	FEED
0.89072E+00		0.91843E-01	0.38892E-02		0.18038E-02	0.38469E-03	0.23080E-04	0.65843E-02	0.47545E-02	PRODUCT

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI10E	,04/12/80,	1.4761	593.1	0.6079	0.5929E-01	1.46	0.03188				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.89088E+00	0.96578E-01	0.0		0.0	0.40484E-03	0.24673E-04	0.70120E-02	0.51004E-02	FEED	
	0.89049E+00	0.93459E-01	0.28479E-02		0.12557E-02	0.39966E-03	0.23986E-04	0.67130E-02	0.48086E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI10F	,12/12/80,	1.4721	591.1	0.6079	0.2327E-01	3.89	0.06787				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.89479E+00	0.92684E-01	0.0		0.0	0.37789E-03	0.23255E-04	0.69392E-02	0.51832E-02	FEED	
	0.89380E+00	0.86298E-01	0.59318E-02		0.27017E-02	0.36754E-03	0.21880E-04	0.63155E-02	0.45633E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI10G	,12/12/80,	1.4709	591.1	0.6079	0.2987E-01	3.00	0.05797				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.89390E+00	0.93607E-01	0.0		0.0	0.37742E-03	0.23217E-04	0.69249E-02	0.51703E-02	FEED	
	0.89305E+00	0.88097E-01	0.50247E-02		0.24107E-02	0.36856E-03	0.22036E-04	0.63884E-02	0.46361E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12A	,20/11/80,	1.4617	593.1	0.6079	0.1552E-01	4.70	0.09136				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.87192E+00	0.11602E+00	0.0		0.0	0.39727E-03	0.23997E-04	0.67593E-02	0.48729E-02	FEED	
	0.87179E+00	0.10541E+00	0.88695E-02		0.36997E-02	0.38018E-03	0.21814E-04	0.58369E-02	0.39973E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12B	,25/11/80,	1.4555	592.1	0.6079	0.2366E-01	3.13	0.06652				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.87293E+00	0.11458E+00	0.0		0.0	0.38731E-03	0.23787E-04	0.69464E-02	0.51346E-02	FEED	
	0.87217E+00	0.10686E+00	0.67883E-02		0.31309E-02	0.37496E-03	0.22159E-04	0.62268E-02	0.44290E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12C	,25/11/80,	1.4731	592.1	0.6079	0.3074E-01	2.38	0.03074				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.87292E+00	0.11491E+00	0.0		0.0	0.38756E-03	0.23535E-04	0.67955E-02	0.49667E-02	FEED	
	0.87252E+00	0.11133E+00	0.31301E-02		0.15324E-02	0.38172E-03	0.22767E-04	0.64567E-02	0.46350E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12D	,03/12/80,	1.4747	592.1	0.6079	0.4602E-01	1.55	0.03831				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.87034E+00	0.11719E+00	0.0		0.0	0.39071E-03	0.23891E-04	0.69466E-02	0.51125E-02	FEED	
	0.86991E+00	0.11264E+00	0.39784E-02		0.18454E-02	0.38353E-03	0.22941E-04	0.65250E-02	0.46976E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12E	,04/12/80,	1.4749	593.1	0.6079	0.5902E-01	1.25	0.03285				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.87374E+00	0.11366E+00	0.0		0.0	0.40526E-03	0.24743E-04	0.70449E-02	0.51337E-02	FEED	
	0.87330E+00	0.10987E+00	0.33115E-02		0.16365E-02	0.39903E-03	0.23916E-04	0.66847E-02	0.47819E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12F	,12/12/80,	1.4709	591.1	0.6079	0.2363E-01	2.87	0.06362				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.86390E+00	0.12375E+00	0.0		0.0	0.37606E-03	0.23050E-04	0.68504E-02	0.50964E-02	FEED	
	0.86296E+00	0.11575E+00	0.71712E-02		0.32902E-02	0.36321E-03	0.21363E-04	0.60927E-02	0.43497E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WI12G	,12/12/80	1.4697	591.1	0.6079	0.2999E-01	2.30	0.05043				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.86558E+00	0.12197E+00	0.0		0.0	0.37685E-03	0.23165E-04	0.69046E-02	0.51515E-02	FEED	
	0.86484E+00	0.11572E+00	0.55876E-02		0.25909E-02	0.36702E-03	0.21863E-04	0.63147E-02	0.45656E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15A	,20/11/80,	1.4617	593.1	0.6079	0.1553E-01	3.83	0.07817			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.84546E+00	0.14248E+00	0.0	0.0	0.39732E-03	0.24003E-04	0.67618E-02	0.48753E-02	FEED	
	0.84448E+00	0.13119E+00	0.98420E-02	0.45164E-02	0.37755E-03	0.21483E-04	0.57002E-02	0.38711E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15B	,22/11/80,	1.4555	591.1	0.6079	0.2358E-01	2.52	0.06148			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.84446E+00	0.14305E+00	0.0	0.0	0.37462E-03	0.23116E-04	0.69160E-02	0.51797E-02	FEED	
	0.84376E+00	0.13414E+00	0.77365E-02	0.35035E-02	0.36102E-03	0.21323E-04	0.61063E-02	0.43774E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15C	,25/11/80,	1.4731	593.1	0.6079	0.3070E-01	1.95	0.02909			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.84714E+00	0.14063E+00	0.0	0.0	0.40118E-03	0.24281E-04	0.68528E-02	0.49501E-02	FEED	
	0.84672E+00	0.13647E+00	0.35963E-02	0.17596E-02	0.39423E-03	0.23371E-04	0.64609E-02	0.45714E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15D	,03/12/80,	1.4723	593.1	0.6079	0.4711E-01	1.27	0.01844			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.84663E+00	0.14109E+00	0.0	0.0	0.40152E-03	0.24334E-04	0.68773E-02	0.49746E-02	FEED	
	0.84437E+00	0.13811E+00	0.41926E-02	0.19710E-02	0.39353E-03	0.23266E-04	0.64144E-02	0.45262E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15E	,04/12/80,	1.4726	593.1	0.6079	0.5914E-01	0.95	0.02700			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.83803E+00	0.14937E+00	0.0	0.0	0.40473E-03	0.24718E-04	0.70398E-02	0.51315E-02	FEED	
	0.83768E+00	0.14528E+00	0.35481E-02	0.16484E-02	0.39817E-03	0.23850E-04	0.66621E-02	0.47628E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WI15G	,12/12/80,	1.4697	591.1	0.6079	0.3116E-01	1.96	0.04323			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.85017E+00	0.13783E+00	0.0	0.0	0.37270E-03	0.22661E-04	0.66805E-02	0.49301E-02	FEED		
0.84952E+00	0.13177E+00	0.53988E-02	0.24458E-02	0.36296E-03	0.21389E-04	0.61116E-02	0.43714E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WT6HA,	14/12/80,	1.4677	653.1	0.6079	0.1759E-01	8.80	0.23271				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.92628E+00	0.60065E-01	0.0		0.0	0.24010E-02	0.11172E-03	0.82634E-02	0.28819E-02	FEED	
	0.92589E+00	0.46068E-01	0.11848E-01		0.52381E-02	0.22358E-02	0.95795E-04	0.65246E-02	0.20953E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WT6HB,	14/12/80,	1.4712	653.1	0.6079	0.2720E-01	5.90	0.18593				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.92841E+00	0.57703E-01	0.0		0.0	0.24191E-02	0.11313E-03	0.84100E-02	0.29478E-02	FEED	
	0.92810E+00	0.46959E-01	0.91000E-02		0.40294E-02	0.22970E-02	0.10115E-03	0.70804E-02	0.23369E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WT6HC,	14/12/80,	1.4701	653.1	0.6079	0.3462E-01	4.54	0.19119				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.92703E+00	0.58999E-01	0.0		0.0	0.24226E-02	0.11355E-03	0.84607E-02	0.29723E-02	FEED	
	0.92688E+00	0.47711E-01	0.95403E-02		0.40417E-02	0.22969E-02	0.10120E-03	0.70874E-02	0.23404E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WT6HD,	14/12/80,	1.4630	653.1	0.6079	0.5302E-01	2.95	0.14257				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.92645E+00	0.59485E-01	0.0		0.0	0.24210E-02	0.11394E-03	0.85245E-02	0.30070E-02	FEED	
	0.92631E+00	0.50997E-01	0.71115E-02		0.31298E-02	0.23288E-02	0.10477E-03	0.74929E-02	0.25266E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV				
WT6HE,	14/12/80,	1.4712	653.1	0.6079	0.6873E-01	2.32	0.12033				
	N2	WATER	H2S		SO2	S2	S4	S6	S8		
	0.92800E+00	0.58035E-01	0.0		0.0	0.24238E-02	0.11357E-03	0.84594E-02	0.29709E-02	FEED	
	0.92788E+00	0.51046E-01	0.58655E-02		0.25650E-02	0.23478E-02	0.10602E-03	0.76100E-02	0.25756E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6MA,	15/12/80,	1.4710	624.1	0.6079	0.1700E-01	8.32	0.19677			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.92496E+00	0.62727E-01	0.0	0.0	0.10531E-02	0.55081E-04	0.75400E-02	0.36678E-02	FEED	
	0.92353E+00	0.50307E-01	0.11172E-01	0.51468E-02	0.98678E-03	0.47835E-04	0.60691E-02	0.27363E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6MB,	15/12/80,	1.4710	624.1	0.6079	0.2610E-01	5.50	0.15535			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.92566E+00	0.61704E-01	0.0	0.0	0.10617E-02	0.55980E-04	0.77250E-02	0.37882E-02	FEED	
	0.92552E+00	0.52111E-01	0.80009E-02	0.34606E-02	0.10177E-02	0.51069E-04	0.67074E-02	0.31305E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6MC,	15/12/80,	1.4651	624.1	0.6079	0.3347E-01	4.57	0.13203			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.92926E+00	0.58092E-01	0.0	0.0	0.10594E-02	0.55957E-04	0.77359E-02	0.38004E-02	FEED	
	0.92930E+00	0.50424E-01	0.64580E-02	0.25176E-02	0.10255E-02	0.52157E-04	0.69426E-02	0.32840E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6MD,	15/12/80,	1.4639	624.1	0.6079	0.4919E-01	3.35	0.10042			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93284E+00	0.53953E-01	0.0	0.0	0.10736E-02	0.57503E-04	0.80613E-02	0.40159E-02	FEED	
	0.93274E+00	0.48530E-01	0.46025E-02	0.18902E-02	0.10504E-02	0.54832E-04	0.74917E-02	0.36374E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6ME,	15/12/80,	1.4639	624.1	0.6079	0.6687E-01	2.29	0.07619			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.92934E+00	0.58065E-01	0.0	0.0	0.10573E-02	0.55784E-04	0.77031E-02	0.37800E-02	FEED	
	0.92923E+00	0.53635E-01	0.36940E-02	0.16500E-02	0.10374E-02	0.53537E-04	0.72312E-02	0.34707E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LA,	20/11/80,	1.4648	591.1	0.6079	0.1538E-01	9.49	0.11416			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93012E+00	0.57800E-01	0.0	0.0	0.37250E-03	0.22711E-04	0.67140E-02	0.49685E-02	FEED	
	0.92850E+00	0.51112E-01	0.66044E-02	0.31232E-02	0.36044E-03	0.21126E-04	0.60039E-02	0.42712E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LB,	22/11/80,	1.4531	591.1	0.6079	0.2376E-01	6.57	0.09410			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93326E+00	0.54334E-01	0.0	0.0	0.37339E-03	0.23002E-04	0.68705E-02	0.51371E-02	FEED	
	0.93353E+00	0.49235E-01	0.37886E-02	0.18505E-02	0.36677E-03	0.22123E-04	0.64704E-02	0.47372E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LC,	25/11/80,	1.4743	591.1	0.6079	0.3046E-01	5.10	0.04214			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93384E+00	0.53927E-01	0.0	0.0	0.37563E-03	0.22946E-04	0.67963E-02	0.50391E-02	FEED	
	0.93322E+00	0.51620E-01	0.22918E-02	0.11339E-02	0.37155E-03	0.22400E-04	0.65480E-02	0.47915E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LD,	03/12/80,	1.4664	593.1	0.6079	0.4621E-01	3.45	0.05878			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93453E+00	0.52939E-01	0.0	0.0	0.40290E-03	0.24598E-04	0.70034E-02	0.51033E-02	FEED	
	0.93367E+00	0.49781E-01	0.32934E-02	0.14133E-02	0.39699E-03	0.23808E-04	0.66583E-02	0.47659E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LE,	04/12/80,	1.4702	593.1	0.6079	0.5962E-01	2.52	0.04911			
	N2	WATER	H2S	SO2	S2	S4	S6	S8		
	0.93131E+00	0.56162E-01	0.0	0.0	0.40353E-03	0.24612E-04	0.70000E-02	0.50956E-02	FEED	
	0.93075E+00	0.53371E-01	0.27672E-02	0.11650E-02	0.39860E-03	0.23954E-04	0.67127E-02	0.48146E-02	PRODUCT	

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LF,	12/12/80,	1.4709	591.1	0.6079	0.2350E-01	6.30	0.06265			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93082E+00	0.56752E-01	0.0	0.0	0.37679E-03	0.23140E-04	0.68903E-02	0.51360E-02	FEED		
0.92899E+00	0.53092E-01	0.44274E-02	0.20132E-02	0.36913E-03	0.22106E-04	0.64192E-02	0.46661E-02	PRODUCT		

RUN	DATE	PRESS	TEMP	WT CAT	S.V.	WT/FA	CONV			
WT6LG,	12/12/80,	1.4697	591.1	0.6079	0.2981E-01	5.71	0.06596			
N2	WATER	H2S	SO2	S2	S4	S6	S8			
0.93809E+00	0.49378E-01	0.0	0.0	0.37754E-03	0.23250E-04	0.69425E-02	0.51893E-02	FEED		
0.93701E+00	0.46068E-01	0.34534E-02	0.16851E-02	0.37153E-03	0.22437E-04	0.65702E-02	0.48160E-02	PRODUCT		

Results of Fitting Experimental Data to the Tanh Function

The identifying code for each data set was illustrated at the beginning of the last section. A summary of the experimental conditions at which the data was obtained is given. The average percentage deviation from the mean value is given after the '#' sign. The factors by which the experimental data have been scaled in order for the program to run are noted next. These will affect the actual value of the slope at the origin. The estimates of the parameters A and B follow. The initial guess of the parameters is recorded since it is necessary to determine that the solution is the global rather than the local minimisation of the sums of squares. It should be noted too, that the actual value of the weighted sum of squares is dependent on the scaling factors.

The table that follows lists the experimental data and the least squares estimate of the dependent variable. The X values are the scaled inverse mol feed rates. The Y values are the scaled conversions

DATA SET SI04

TEMPERATURE = 591.2 K # 0.0
PRESSURE = 1.4767 ATM # 0.1300

SULPHUR 0.17840 % # 4.00000
WATER 2.06620 % # 6.70000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1385E+00 0.5300E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1388E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.4450E-01	0.4630E-01	0.1000E+01	0.6284E+00
0.5601E-01	0.5861E-01	0.1000E+01	0.8091E+00
0.8131E-01	0.8760E-01	0.1000E+01	0.1270E+01
0.9840E-01	0.9035E-01	0.1000E+01	0.1675E+01
0.1125E+00	0.1090E+00	0.1000E+01	0.2137E+01
0.1309E+00	0.1343E+00	0.1000E+01	0.3361E+01

DATA SET SI05

TEMPERATURE = 592.3 K # 0.1
PRESSURE = 1.4789 ATM # 0.1500

SULPHUR 0.24325 % # 6.12000
WATER 2.69740 % # 10.82000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1370E+00 0.6201E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.4806E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.6254E-01	0.6102E-01	0.1000E+01	0.7951E+00
0.4925E-01	0.5416E-01	0.1000E+01	0.6070E+00
0.1169E+00	0.1129E+00	0.1000E+01	0.2044E+01
0.1317E+00	0.1342E+00	0.1000E+01	0.3177E+01

DATA SET SI06

TEMPERATURE = 591.4 K # 0.1
PRESSURE = 1.4813 ATM # 0.1300

SULPHUR 0.29798 % # 2.21000
WATER 2.54520 % # 13.87000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1247E+00 0.8152E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.4640E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.3749E-01	0.4059E-01	0.1000E+01	0.3807E+00
0.5554E-01	0.5022E-01	0.1000E+01	0.5876E+00
0.6783E-01	0.7074E-01	0.1000E+01	0.7481E+00
0.9373E-01	0.9353E-01	0.1000E+01	0.1198E+01

DATA SET SI08

TEMPERATURE = 592.0 K # 0.2
PRESSURE = 1.4755 ATM # 0.3600

SULPHUR 0.40130 % # 3.20000
WATER 2.15840 % # 10.40000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.9107E-01 0.9947E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2329E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.3212E-01	0.4017E-01	0.1000E+01	0.3705E+00
0.4607E-01	0.4946E-01	0.1000E+01	0.5601E+00
0.5590E-01	0.5732E-01	0.1000E+01	0.7189E+00
0.5761E-01	0.5447E-01	0.1000E+01	0.7496E+00
0.6794E-01	0.6168E-01	0.1000E+01	0.9692E+00
0.8193E-01	0.8018E-01	0.1000E+01	0.1478E+01
0.8688E-01	0.8744E-01	0.1000E+01	0.1885E+01
0.8940E-01	0.8642E-01	0.1000E+01	0.2354E+01
0.8935E-01	0.8770E-01	0.1000E+01	0.2338E+01
0.9106E-01	0.8870E-01	0.1000E+01	0.4695E+01
0.9069E-01	0.9990E-01	0.1000E+01	0.3100E+01

DATA SET SI10

TEMPERATURE = 592.0 K # 3.6
PRESSURE = 1.4680 ATM # 0.1000

SULPHUR 0.60076 % # 3.60000
WATER 2.39120 % # 14.10000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.7081E-01 0.1658E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1603E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.3023E-01	0.3038E-01	0.1000E+01	0.2751E+00
0.3682E-01	0.4138E-01	0.1000E+01	0.3476E+00
0.4523E-01	0.4327E-01	0.1000E+01	0.4560E+00
0.5036E-01	0.5607E-01	0.1000E+01	0.5365E+00
0.5820E-01	0.5086E-01	0.1000E+01	0.7012E+00
0.6412E-01	0.6182E-01	0.1000E+01	0.9058E+00
0.6964E-01	0.6676E-01	0.1000E+01	0.1443E+01
0.7043E-01	0.6970E-01	0.1000E+01	0.1787E+01
0.7072E-01	0.7620E-01	0.1000E+01	0.2230E+01
0.7073E-01	0.6969E-01	0.1000E+01	0.2246E+01
0.7080E-01	0.7080E-01	0.1000E+01	0.2882E+01
0.7081E-01	0.7280E-01	0.1000E+01	0.4437E+01

DATA SET SI15

TEMPERATURE = 591.5 K # 0.1
PRESSURE = 1.4729 ATM # 0.6500

SULPHUR 0.90153 % # 6.91000
WATER 2.38710 % # 6.60000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.5499E-01 0.2567E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2129E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2198E-01	0.2474E-01	0.1000E+01	0.1649E+00
0.3151E-01	0.3121E-01	0.1000E+01	0.2540E+00
0.4443E-01	0.4405E-01	0.1000E+01	0.4366E+00
0.5163E-01	0.4725E-01	0.1000E+01	0.6730E+00
0.5373E-01	0.5543E-01	0.1000E+01	0.8681E+00
0.5491E-01	0.5864E-01	0.1000E+01	0.1385E+01
0.5499E-01	0.5741E-01	0.1000E+01	0.2133E+01
0.5499E-01	0.5131E-01	0.1000E+01	0.2754E+01
0.5488E-01	0.5760E-01	0.1000E+01	0.1336E+01
0.4750E-01	0.3790E-01	0.1000E+01	0.5094E+00
0.3842E-01	0.4550E-01	0.1000E+01	0.3368E+00

DATA SET SI20

TEMPERATURE = 591.5 K # 0.1
PRESSURE = 1.4590 ATM # 0.4300

SULPHUR 1.25030 % # 2.00000
WATER 2.69050 % # 4.30000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.4586E-01 0.3516E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.9622E-06

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2320E-01	0.2271E-01	0.1000E+01	0.1585E+00
0.3194E-01	0.3271E-01	0.1000E+01	0.2447E+00
0.3709E-01	0.3673E-01	0.1000E+01	0.3196E+00

DATA SET SI25

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4795 ATM # 0.3600

SULPHUR 1.36260 % # 4.10000
WATER 2.51840 % # 8.00000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.3802E-01 0.4459E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.3802E-17

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2324E-01	0.2324E-01	0.1000E+01	0.1594E+00
0.3364E-01	0.3364E-01	0.1000E+01	0.3135E+00

DATA SET SI30

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.5825 ATM # 0.0600

SULPHUR 1.75200 % # 0.90000
WATER 2.21460 % # 13.90000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.3353E-01 0.5365E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1147E-05

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2280E-01	0.2239E-01	0.1000E+01	0.1545E+00
0.2866E-01	0.2952E-01	0.1000E+01	0.2374E+00
0.3111E-01	0.3062E-01	0.1000E+01	0.3060E+00

DATA SET SI35

TEMPERATURE = 593.2 K # 0.0
PRESSURE = 1.4776 ATM # 0.1000

SULPHUR 2.00550 % # 2.70000
WATER 2.57770 % # 7.20000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E-01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.2937E-01 0.6353E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.8954E-07

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2192E-01	0.2182E-01	0.1000E+01	0.1519E+00
0.2655E-01	0.2679E-01	0.1000E+01	0.2351E+00
0.2818E-01	0.2803E-01	0.1000E+01	0.3052E+00

DATA SET WI01

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4722 ATM # 0.3100

SULPHUR 0.50240 % # 2.10000
WATER 1.03250 % # 1.00000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1262E+00 0.5544E-01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2397E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.8120E-01	0.8434E-01	0.1000E+01	0.1378E+02
0.9439E-01	0.9576E-01	0.1000E+01	0.1746E+02
0.1150E+00	0.1115E+00	0.1000E+01	0.2769E+02
0.1218E+00	0.1208E+00	0.1000E+01	0.3639E+02
0.1250E+00	0.1357E+00	0.1000E+01	0.4769E+02
0.1212E+00	0.1113E+00	0.1000E+01	0.3517E+02

DATA SET WI02

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4708 ATM # 0.3400

SULPHUR 0.48652 % # 8.50000
WATER 1.93550 % # 7.80000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+00

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1218E+00 0.7327E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2098E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.5680E-01	0.5877E-01	0.1000E+01	0.6900E+00
0.7521E-01	0.7568E-01	0.1000E+01	0.9844E+00
0.9493E-01	0.9618E-01	0.1000E+01	0.1425E+01
0.9717E-01	0.9950E-01	0.1000E+01	0.1492E+01
0.1085E+00	0.1044E+00	0.1000E+01	0.1947E+01
0.1088E+00	0.9873E-01	0.1000E+01	0.1963E+01
0.1153E+00	0.1243E+00	0.1000E+01	0.2455E+01

DATA SET WI04

TEMPERATURE = 592.4 K # 0.2
PRESSURE = 1.4721 ATM # 0.3200

SULPHUR 0.49985 % # 1.70000
WATER 3.68195 % # 6.10000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+00

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1197E+00 0.1127E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1233E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.4875E-01	0.5012E-01	0.1000E+01	0.3837E+00
0.6558E-01	0.6358E-01	0.1000E+01	0.5460E+00
0.8198E-01	0.8381E-01	0.1000E+01	0.7438E+00
0.9807E-01	0.9644E-01	0.1000E+01	0.1025E+01
0.1097E+00	0.1104E+00	0.1000E+01	0.1391E+01

DATA SET WI06

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4637 ATM # 0.5000

SULPHUR 0.50760 % # 1.50000
WATER 5.53100 % # 3.80000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1272E+00 0.1496E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1837E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.4572E-01	0.4911E-01	0.1000E+01	0.2516E+01
0.6042E-01	0.5878E-01	0.1000E+01	0.3453E+01
0.9588E-01	0.9410E-01	0.1000E+01	0.6563E+01
0.1131E+00	0.1142E+00	0.1000E+01	0.9490E+01

DATA SET WI08

TEMPERATURE = 592.0 K # 0.2
PRESSURE = 1.4666 ATM # 0.6300

SULPHUR 0.52170 % # 5.10000
WATER 7.35400 % # 5.40000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.9271E-01 0.2442E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2882E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.3944E-01	0.4358E-01	0.1000E+01	0.1860E+01
0.5183E-01	0.5138E-01	0.1000E+01	0.2586E+01
0.6667E-01	0.6405E-01	0.1000E+01	0.3709E+01
0.7972E-01	0.7834E-01	0.1000E+01	0.5294E+01
0.8865E-01	0.9029E-01	0.1000E+01	0.7779E+01

DATA SET WI12

TEMPERATURE = 592.0 K # 0.1
PRESSURE = 1.4692 ATM # 0.5400

SULPHUR 0.51258 % # 0.40000
WATER 11.82300 % # 3.80000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1198E+00 0.2051E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1657E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.3009E-01	0.3285E-01	0.1000E+01	0.1252E+01
0.3695E-01	0.3831E-01	0.1000E+01	0.1555E+01
0.5258E-01	0.5043E-01	0.1000E+01	0.2296E+01
0.6352E-01	0.6362E-01	0.1000E+01	0.2880E+01
0.6790E-01	0.6652E-01	0.1000E+01	0.3134E+01
0.8939E-01	0.9014E-01	0.1000E+01	0.4702E+01

DATA SET WI15

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4677 ATM # 0.3300

SULPHUR 0.50290 % # 3.00000
WATER 14.31800 % # 3.30000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1069E+00 0.2447E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.3402E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2446E-01	0.2700E-01	0.1000E+01	0.9519E+00
0.4759E-01	0.4323E-01	0.1000E+01	0.1956E+01
0.5858E-01	0.6148E-01	0.1000E+01	0.2515E+01
0.7848E-01	0.7817E-01	0.1000E+01	0.3831E+01

DATA SET WI10

TEMPERATURE = 591.8 K # 0.1
PRESSURE = 1.4695 ATM # 0.6300

SULPHUR 0.51620 % # 0.70000
WATER 9.39510 % # 2.60000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1883E+00 0.1046E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1086E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.2864E-01	0.3187E-01	0.1000E+01	0.1465E+01
0.3714E-01	0.4456E-01	0.1000E+01	0.1910E+01
0.5727E-01	0.5797E-01	0.1000E+01	0.3002E+01
0.7267E-01	0.6787E-01	0.1000E+01	0.3890E+01
0.7412E-01	0.7024E-01	0.1000E+01	0.3976E+01
0.1092E+00	0.1113E+00	0.1000E+01	0.6330E+01

DATA SET WT6L

TEMPERATURE = 592.2 K # 0.2
PRESSURE = 1.4637 ATM # 0.5000

SULPHUR 0.50800 % # 1.18000
WATER 5.53190 % # 3.09000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1271E+00 0.1498E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1917E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.1131E+00	0.1142E+00	0.1000E+01	0.9480E+01
0.9596E-01	0.9410E-01	0.1000E+01	0.6570E+01
0.6041E-01	0.5877E-01	0.1000E+01	0.3450E+01
0.4566E-01	0.4911E-01	0.1000E+01	0.2510E+01
0.0	0.0	0.1000E+01	0.0

DATA SET WT6M

TEMPERATURE = 624.3 K # 1.0
PRESSURE = 1.4670 ATM # 0.5000

SULPHUR 0.38104 % # 2.97000
WATER 5.89080 % # 5.28000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.2441E+00 0.1346E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.2454E-04

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.0	0.0	0.1000E+01	0.0
0.1970E+00	0.1968E+00	0.1000E+01	0.8310E+01
0.1534E+00	0.1553E+00	0.1000E+01	0.5490E+01
0.1337E+00	0.1320E+00	0.1000E+01	0.4570E+01
0.1031E+00	0.1004E+00	0.1000E+01	0.3350E+01
0.7293E-01	0.7618E-01	0.1000E+01	0.2290E+01

DATA SET WT6H

TEMPERATURE = 653.2 K # 1.0
PRESSURE = 1.4687 ATM # 0.5000

SULPHUR 0.29560 % # 1.40000
WATER 5.88570 % # 1.49000

SCALING FACTORS
CONVERSION * 0.10000E+01
PARTIAL PRESSURE * 0.10000E+01

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.2296E+00 0.2437E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.5185E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.2231E+00	0.2327E+00	0.1000E+01	0.8710E+01
0.1841E+00	0.1912E+00	0.1000E+01	0.4530E+01
0.1415E+00	0.1426E+00	0.1000E+01	0.2950E+01
0.1175E+00	0.1203E+00	0.1000E+01	0.2320E+01
0.0	0.0	0.1000E+01	0.0
0.2051E+00	0.1859E+00	0.1000E+01	0.5900E+01

Results of Estimating the Water Dependence of the Reaction

This section follows the format of the previous one. In this instance, the X values are the partial pressures of water. The Y values are the rates of reaction with respect to water. The particular form of the rate equation that is being fitted is given after the data summary at the top of each page. The parameters, C, N and K are estimated in that order by the program.

DATA SET WRATE

TEMPERATURE = 592.1 K # 0.170
PRESSURE = 1.4684 ATM # 0.0

SULPHUR 0.50622 % # 2.90000
WATER 0.0 % # 4.90000

Y = C*W**N/((1+K*W)**0.0)

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 2 PARAMETERS ARE:

0.1930E+00 0.4885E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1764E-02

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.7731E-01	0.6996E-01	0.1000E+01	0.1536E+00
0.1051E+00	0.8924E-01	0.1000E+01	0.2880E+00
0.1439E+00	0.1349E+00	0.1000E+01	0.5479E+00
0.1755E+00	0.1903E+00	0.1000E+01	0.8230E+00
0.2028E+00	0.2264E+00	0.1000E+01	0.1106E+01
0.2274E+00	0.2420E+00	0.1000E+01	0.1398E+01
0.2544E+00	0.2457E+00	0.1000E+01	0.1759E+01
0.2793E+00	0.2616E+00	0.1000E+01	0.2131E+01

DATA SET WRATE

TEMPERATURE = 592.1 K # 0.170
PRESSURE = 1.4684 ATM # 0.100

SULPHUR 0.50622 % # 2.90000
WATER 0.0 % # 4.90000

Y = C*W**N/((1+K*W)**0.5)

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 3 PARAMETERS ARE:

0.2839E+00 0.7196E+00 0.1040E+01

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.1032E-02

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.6847E-01	0.6996E-01	0.1000E+01	0.1536E+00
0.1017E+00	0.8924E-01	0.1000E+01	0.2880E+00
0.1470E+00	0.1349E+00	0.1000E+01	0.5479E+00
0.1811E+00	0.1903E+00	0.1000E+01	0.8230E+00
0.2082E+00	0.2264E+00	0.1000E+01	0.1106E+01
0.2306E+00	0.2420E+00	0.1000E+01	0.1398E+01
0.2534E+00	0.2457E+00	0.1000E+01	0.1759E+01
0.2728E+00	0.2616E+00	0.1000E+01	0.2131E+01

DATA SET WRATE

TEMPERATURE = 592.1 K # 0.170
PRESSURE = 1.4684 ATM # 0.100

SULPHUR 0.50622 % # 2.90000
WATER 0.0 % # 4.90000

Y = C*W**N/((1+K*W)**1.0)

0

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 3 PARAMETERS ARE:

0.3557E+00 0.8790E+00 0.7461E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.6907E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.6149E-01	0.6996E-01	0.1000E+01	0.1536E+00
0.9803E-01	0.8924E-01	0.1000E+01	0.2880E+00
0.1488E+00	0.1349E+00	0.1000E+01	0.5479E+00
0.1857E+00	0.1903E+00	0.1000E+01	0.8230E+00
0.2129E+00	0.2264E+00	0.1000E+01	0.1106E+01
0.2337E+00	0.2420E+00	0.1000E+01	0.1398E+01
0.2527E+00	0.2457E+00	0.1000E+01	0.1759E+01
0.2671E+00	0.2616E+00	0.1000E+01	0.2131E+01

DATA SET WRATE

TEMPERATURE = 592.1 K # 0.170
PRESSURE = 1.4684 ATM # 0.100

SULPHUR 0.50622 % # 2.90000
WATER 0.0 % # 4.90000

Y = C*W**N/((1+K*W)**2.0)

0

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 3 PARAMETERS ARE:

0.3358E+00 0.8911E+00 0.2742E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.5449E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.5824E-01	0.6996E-01	0.1000E+01	0.1536E+00
0.9513E-01	0.8924E-01	0.1000E+01	0.2880E+00
0.1485E+00	0.1349E+00	0.1000E+01	0.5479E+00
0.1879E+00	0.1903E+00	0.1000E+01	0.8230E+00
0.2163E+00	0.2264E+00	0.1000E+01	0.1106E+01
0.2365E+00	0.2420E+00	0.1000E+01	0.1398E+01
0.2528E+00	0.2457E+00	0.1000E+01	0.1759E+01
0.2625E+00	0.2616E+00	0.1000E+01	0.2131E+01

DATA SET WRATE

TEMPERATURE = 592.1 K # 0.170
PRESSURE = 1.4684 ATM # 0.100

SULPHUR	0.50622 %	#	2.90000
WATER	0.0 %	#	4.90000

Y = C*W**N/((1+K*W)**3.0)

NONLINEAR REGRESSION PROGRAM

METHOD OF MEYER AND ROTH FROM THE TEXT OF WOLFE,M.A.
NUMERICAL METHODS FOR UNCONSTRAINED OPTIMIZATION
VAN NOSTRAND REINHOLD, (1978).

ESTIMATES FOR THE 3 PARAMETERS ARE:

0.3215E+00 0.8751E+00 0.1576E+00

THE INITIAL PARAMETER VALUES WERE:

0.5000E+00 0.5000E+00 0.5000E+00

WEIGHTED SUM-OF-SQUARES IS 0.5170E-03

PREDICTED Y	ACTUAL Y	WEIGHTING	X VALUE
0.5808E-01	0.6996E-01	0.1000E+01	0.1536E+00
0.9468E-01	0.8924E-01	0.1000E+01	0.2880E+00
0.1481E+00	0.1349E+00	0.1000E+01	0.5479E+00
0.1881E+00	0.1903E+00	0.1000E+01	0.8230E+00
0.2169E+00	0.2264E+00	0.1000E+01	0.1106E+01
0.2372E+00	0.2420E+00	0.1000E+01	0.1398E+01
0.2530E+00	0.2457E+00	0.1000E+01	0.1759E+01
0.2615E+00	0.2616E+00	0.1000E+01	0.2131E+01